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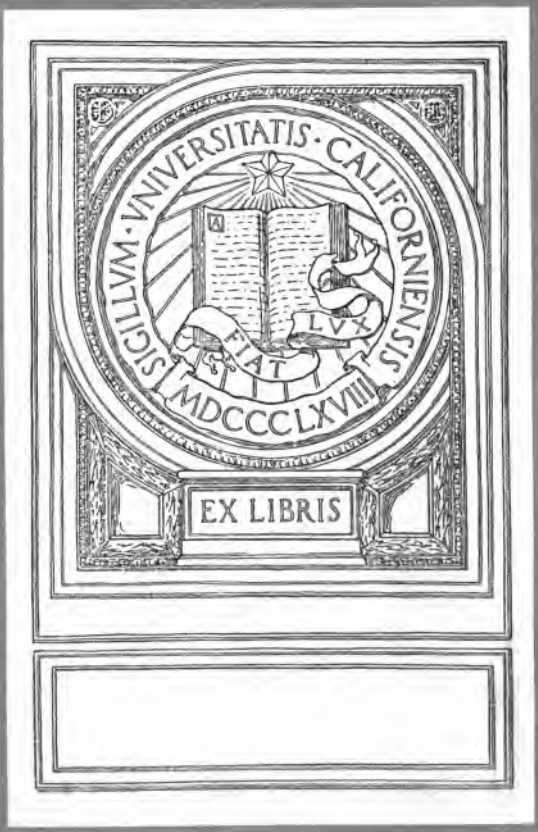
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PHYSICO-CHEMICAL CALCULATIONS

BY

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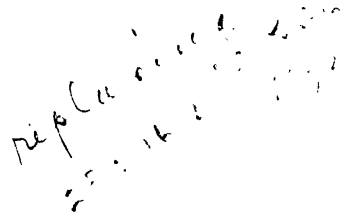

PREFACE

THIS collection of physico-chemical problems is based on Abegg and Sackur's "Physikalisch-Chemische Rechen-aufgaben" (Sammlung Göschen).

The original intention was simply to translate the German book, which consists of a short summary of the laws and formulæ used in the problems, and fifty-two typical problems, with full solutions. With the consent of the late Professor Abegg and of Dr. Sackur, however, I decided to arrange the subject-matter in chapters dealing with the main subdivisions of physical chemistry, and to write a short introduction to each chapter, dealing with the theory involved in the problems. Most of the problems in the "Rechenaufgaben" have been retained, a good many additional solved problems have been introduced, and a collection of problems for solution (with answers) has been added at the end of each chapter. The size of the book has thus been more than doubled.

Most of the problems have been taken direct, or with slight modification, from the original literature.

I shall be grateful to have any errors in the text pointed out to me.

I would take this opportunity of expressing my indebtedness to the late Professor Richard Abegg, and to Dr. Otto Sackur, of the University of Breslau, for their kindness in allowing me to make use of their "Rechenaufgaben" as the basis of this book.

J. K.

ABERDEEN,
December, 1911.

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PHYSICO-CHEMICAL CALCULATIONS

CHAPTER I

GAS LAWS—GASEOUS DISSOCIATION—OSMOTIC PRESSURE

Gas Laws

THE relation between the pressure, volume and temperature of any given mass of gas is expressed by the equation

$$(1)\ \frac{Pv}{T} = \frac{P'v'}{T'}$$

where P and v are the pressure and volume corresponding to the absolute temperature T and P' and v' the pressure and volume corresponding to the absolute temperature T'. The absolute temperature is equal to $273 + t$, where t is the temperature centigrade. The pressure and volume may be expressed in any units.

This relation may also be expressed in the form

$$\frac{Pv}{T} = \text{constant, or } Pv = \text{constant} \times T.$$

The value of the constant varies with the units of pressure and volume and with the mass of gas considered. For the gram-molecular quantity of all gases, however, the value of the constant is the same. For a gram-molecule of a gas the equation, therefore, becomes

$$Pv = RT,$$

and for n gram-molecules

$$(2)\ Pv = nRT \text{ (Boyle, Gay-Lussac, Avogadro).}$$

P is the pressure of the gas, n the number of gram-molecules or moles present in the volume v, R the gas-constant and T the absolute temperature. The numerical value of R varies with the units of pressure and volume adopted. If we take the atmosphere as the unit of pressure and the litre as the unit of volume, we obtain the corresponding value of R from the fact that one gram-molecule of any gas ($n = 1$) occupies 22·4 litres at 0° C. (273° absolute) and under a pressure of one atmosphere. Then, from (2),

$$1 \times 22{\cdot}4 = 1 \times R \times 273 \therefore R = \frac{22{\cdot}4}{273} = 0{\cdot}08204.$$

If the pressure is given in millimetres of mercury and the volume in cubic centimetres, the former must be divided by 760 to convert it to atmospheres and the latter by 1000 to convert it to litres before this value of R can be used.

If the total pressure P of a mixture of gases is replaced by the partial pressure p of any of its components, the same equations hold for each individual gas in the mixture, of which the total volume is v (Dalton's law).

Osmotic Pressure

For the osmotic pressure π of a dilute solution of volume v, equations exactly analogous to the gas-equations hold, namely,

$$(3)\quad \frac{\pi v}{T} = \frac{\pi' v'}{T'},$$

and

$$(4)\quad \pi v = nRT.$$

π is the osmotic pressure, n the number of gram-molecules of dissolved substance in the volume v of solution, T the absolute temperature and R a constant, the value of which is the same as in the gas-equation and numerically equal to 0·08204 if π is measured in atmospheres and v in litres. The last equation may be written in the form:

$$\pi = \frac{nRT}{v} = RTc,$$

where c is the concentration of the dissolved substance, (e.g. gram-molecules per litre, if the above units are adopted).

Gas Laws—Examples

PROBLEM 1.—At $t' = 10°$ C. and under a pressure of $P' = 650$ mm. of mercury a certain mass of hydrogen occupies a volume of $v' = 200$ c.c. What volume, v, will it occupy at $t = 0°$ C. and $P = 760$ mm. pressure?

SOLUTION 1.—Substituting the numerical values in equation (1) we obtain

$$\frac{760 \times v}{273} = \frac{650 \times 200}{283},$$

$$\therefore v = \frac{650 \times 200 \times 273}{760 \times 283} = \mathbf{165} \text{ c.c.}$$

PROBLEM 2.—What volume will $a = 1$ gram of oxygen occupy at a temperature $t = 100°$ C. and under a pressure $P = 740$ mm. of mercury?

SOLUTION 2.—If M is the molecular weight of oxygen, the number of gram-molecules present is $n = \frac{a}{M}$. Equation (2), therefore, becomes

$$Pv = \frac{a}{M}RT, \text{ and } v = \frac{aRT}{MP}.$$

$P = \frac{740}{760}$ atmospheres, $M = 32$, $R = 0{\cdot}08204$, $T = 273 + t = 373$. Substituting these values in the above equation we obtain

$$v = \frac{1 \times 0{\cdot}08204 \times 373 \times 760}{32 \times 740} = \mathbf{0{\cdot}9822} \text{ litres.}$$

PROBLEM 3.—The pressure of the atmosphere at the surface of the earth is equal to the weight of a column of mercury 76 cms. high. With increasing height the density of the air diminishes according to Boyle's law. What is the density of the air at the heights $h_1 = 1000$ metres, and $h_2 = 3000$ metres, if the density s_0 at the surface of the earth $= 0{\cdot}00129$? ($t = 0°$ C.).

SOLUTION 3.—According to Boyle's law the volume of a gas at constant temperature is inversely proportional to the pressure on it; its density, i.e. the mass contained in unit volume, is, therefore, directly proportional to the pressure. Let he pressure of the air at the height h metres $= P_h$, and its

density = s. Then, since s is proportional to the pressure P_s

$$(1)\quad s = kP_s.$$

Similarly at the height $h + dh$,

$$(2)\quad s + ds = kP_{s+ds}.$$

The difference of the pressures P_{s+ds} and P_s is equal to the weight of a column of air of height dh (the difference in the two heights), and of unit area of cross-section, since the pressure of a mass of gas is defined as equal to the weight on unit area. Accordingly we have

$$(3)\quad P_s - P_{s+ds} = s\,.\,dh.$$

From (1), (2) and (3) it follows that

$$ds = -k\,.\,s\,.\,dh, \text{ or } d\log_e s = -k\,.\,dh,$$

and, after integration,

$$(4)\quad \log_e s = -kh + \text{constant}.$$

At the height $h = 0$ we have $s = s_0$, the density of the air at the surface of the earth, and (4) becomes

$$\log_e s_0 = \text{constant},$$

and, therefore,

$$(5)\quad \log_e s = -kh + \log_e s_0.$$

From (1) it follows that k is the density of air under unit pressure. The value of k can be calculated from the data given in the problem, i.e. from the value of the density s_0 at a pressure P of 76 cms. of Hg.

Using the cm. and the gram as our units $P = 76 \times 13{\cdot}6$ grams per sq. cm. (13·6 is the density of Hg), and $s_0 = 0{\cdot}00129$ gram per c.c., therefore,

$$k = \frac{0{\cdot}00129}{76 \times 13{\cdot}6} = 0{\cdot}00000125 = 1{\cdot}25 \times 10^{-6}.$$

Then from (5) we get, for the heights $h_1 = 1000$ m. $= 10^5$ cms., and $h_2 = 3000$ m. $= 3 \times 10^5$ cms.,

$$\begin{aligned}\log_e s_1 &= -1{\cdot}25 \times 10^{-6} \times h_1 + \log_e 0{\cdot}00129,\\ &= -1{\cdot}25 \times 10^{-6} \times 10^5 + \log_e 0{\cdot}00129,\end{aligned}$$

and, changing to common logarithms,

$$\log s_1 = -0{\cdot}4343 \times 0{\cdot}125 + \log 0{\cdot}00129,$$
$$= -0{\cdot}0543 + (0{\cdot}111 - 3)$$
$$= 0{\cdot}057 - 3$$
$$\therefore \mathbf{s_1 = o{\cdot}00114.}$$
$$\log_e s_2 = -1{\cdot}25 \times 10^{-6} \times h_2 + \log_e 0{\cdot}00129,$$
$$= -1{\cdot}25 \times 3 \times 10^{-1} + \log_e 0{\cdot}00129,$$
$$\log s_2 = -0{\cdot}163 + (0{\cdot}111 - 3) = 0{\cdot}947 - 4,$$
$$\therefore \mathbf{s_2 = o{\cdot}000885.}$$

If the densities at the heights h_1 and h_2 are referred to the density at the earth's surface as unity, then

$$\mathbf{s_1} = \frac{0\ 00114}{0{\cdot}00129} = \mathbf{o{\cdot}884},$$

$$\text{and } \mathbf{s_2} = \frac{0{\cdot}000885}{0{\cdot}00129} = \mathbf{o{\cdot}686.}$$

PROBLEM 4 (cf. preceding problem).—The volume v of a balloon, which is open below, is 1400 cubic metres. What is its carrying-capacity B at the heights $h_1 = 1000$ m. and $h_2 = 3000$ m. when filled (*a*) with hydrogen, (*b*) with coal gas, if the specific gravity of coal gas relative to air is 0·43, and that of hydrogen 0·0695? (*c*) What must be the volume of a balloon filled with hydrogen, so that its carrying-capacity may be equal to that of the 1400 c.m. balloon filled with coal gas?

SOLUTION 4.—The carrying-capacity of a balloon can be calculated from the principle of Archimedes. The balloon floats in its position of equilibrium when the weight of balloon + gas + car with contents is equal to the weight of the air displaced by them. For a first approximation the volume of the material of the car may be neglected in comparison with the volume of the balloon.

If v is the volume of the completely filled balloon, d the density of the balloon gas at the height h, and s the density of the air at the same height, then the weight of the balloon gas $= v.d$, and that of the displaced air $= v.s$. Therefore the carrying-capacity B of the balloon $= v\,(s - d)$.

Boyle's law holds both for the balloon gas and for air; accordingly $\frac{d_1}{d_0} = \frac{s_1}{s_0}$, where d_1, s_1 are the densities at the height h_1, and d_0, s_0 the densities at the earth's surface. The carrying-capacity B_1 at the height h_1, is, therefore,

$$B_1 = v(s_1 - d_1) = vs_1\left(1 - \frac{d_0}{s_0}\right),$$

and at the height h_2,

$$B_2 = vs_2\left(1 - \frac{d_0}{s_0}\right).$$

(*a*) For hydrogen $\frac{d_0}{s_0} = 0{\cdot}0695$, therefore, since $v = 1400 \times 10^6$ c.c. and $s_1 = 1{\cdot}14 \times 10^{-3}$ (cf. Problem 3), for $h_1 = 1000$ m. $= 10^5$ cm.

$\mathbf{B_1} = 1400 \times 10^6 \times 1{\cdot}14 \times 10^{-3} \times 0{\cdot}93$ gm. $=$ **1484** kg.,

and, similarly,

$\mathbf{B_2} = 1400 \times 10^6 \times 0{\cdot}885 \times 10^{-3} \times 0{\cdot}93$ gm. $=$ **1152** kg.

(*b*) For coal gas $\frac{d_0}{s_0} = 0{\cdot}43$, therefore

$\mathbf{B_1} = 1400 \times 10^6 \times 1{\cdot}14 \times 10^{-3} \times 0{\cdot}57$ gm. $=$ **910** kg.,

$\mathbf{B_2} = 1400 \times 10^6 \times 0{\cdot}885 \times 10^{-3} \times 0{\cdot}57$ gm. $=$ **706** kg.

(*c*) Let the volume of the hydrogen balloon be v_x, then its carrying-capacity $B = v_x s\left(1 - \frac{d_H}{s}\right)$. Similarly, for a coal gas balloon of the same carrying-capacit we have

$$B = vs\left(1 - \frac{d_C}{s}\right).$$

d_H, d_C and s are the densities at *any* given height of hydrogen, coal gas and air respectively. From these two equations we obtain

$$\frac{v_x}{v} = \frac{1 - \frac{d_C}{s}}{1 - \frac{d_H}{s}},$$

and, therefore,

$$\mathbf{v_x} = 1400 \times \frac{1 - 0{\cdot}43}{1 - 0{\cdot}0695} = \frac{1400 \times 0{\cdot}57}{0{\cdot}93} = \mathbf{858}\text{ c.m.}$$

Problem 5 (cf. preceding problem).—If the balloon of 1400 c.m. capacity is filled completely at the earth's surface (*a*) with hydrogen, (*b*) with coal gas, how many grams of gas are in each case lost when it ascends to the heights $h_1 =$

1000 m. and $h_2 = 3000$ m.? How many kilograms of ballast must be thrown out so that the completely filled balloon may rise from its equilibrium position at the height $h_1 =$ 1000 m. to that at $h_2 = 3000$ m., (*c*) when filled with hydrogen, (*d*) when filled with coal gas?

SOLUTION 5.—The weight of gas lost on ascending to the height h_1 is $G_1 = v(d_0 - d_1)$ grams, and on ascending to the height h_2 it is $G_2 = v(d_0 - d_2)$ grams, where d_0, d_1 and d_2 are the densities of the gas at the earth's surface, at the height h_1 and at the height h_2 respectively.

(*a*) For hydrogen

$$d_0 - d_1 = 0{\cdot}0695\ (0{\cdot}00129 - 0{\cdot}00114)$$
$$= 0{\cdot}0695 \times 0{\cdot}00015 = 1{\cdot}04 \times 10^{-5},$$
$$\text{and } d_0 - d_2 = 0{\cdot}0695\ (0{\cdot}00129 - 0{\cdot}000885)$$
$$= 0{\cdot}0695 \times 0{\cdot}000405 = 2{\cdot}81 \times 10^{-5},$$

therefore the loss of weight

$$G_1 = 1400 \times 10^6 \times 1{\cdot}04 \times 10^{-5} \text{ gm.} = \mathbf{14{\cdot}56} \text{ kg.},$$
$$\text{and } G_2 = 1400 \times 10^6 \times 2{\cdot}81 \times 10^{-5} \text{ gm.} = \mathbf{39{\cdot}3} \text{ kg.}$$

(*b*) Similarly, for coal gas

$$G_1 = 1400 \times 10^6 \times 6{\cdot}45 \times 10^{-5} \text{ gm.} = \mathbf{90{\cdot}3} \text{ kg.},$$
$$\text{and } G_2 = 1400 \times 10^6 \times 1{\cdot}74 \times 10^{-5} \text{ gm.} = \mathbf{243{\cdot}5} \text{ kg.}$$

The weight of ballast which must be thrown out is equal to the difference between the carrying-capacities at the heights h_1 and h_2, and is, therefore,

(*c*) for hydrogen, $1484 - 1152 = \mathbf{332}$ kg.
(*d*) for coal gas, $910 - 706 = \mathbf{204}$ kg.

The throwing out of a given weight of ballast has, therefore, more effect on the coal-gas balloon than on the hydrogen balloon.

Gaseous Dissociation—Examples

PROBLEM 6.—At 90° C. the vapour-density of nitrogen peroxide (N_2O_4), is 24·8 (referred to H = 1). Calculate the degree of dissociation into NO_2 molecules at this temperature.

SOLUTION 6.—Let D be the theoretical vapour-density if no dissociation occurred, and d the observed vapour-density. If one molecule of the dissociating substance gives on dissociating n simpler molecules, and if α is the degree of dissociation, then at equilibrium $1 - \alpha$ undissociated molecules and $n\alpha$ simpler molecules are present for every molecule of undissociated substance initially present. The total number of molecules is, therefore, $1 - \alpha + n\alpha = 1 + \alpha(n - 1)$. The volume

occupied by the gram-molecular quantity of undissociated substance is, therefore, $1 + a(n - 1)$ times as great as it would have been, had no dissociation occurred. But the density of a given mass is inversely proportional to the volume, therefore,

$$\frac{D}{d} = \frac{1 + a(n - 1)}{1}$$

and

$$a = \frac{(D - d)}{d(n - 1)}.$$

In the dissociation of N_2O_4 according to the equation

$$N_2O_4 = 2NO_2,$$

$$n = 2,\ D = \frac{N_2O_4}{2} = \frac{92}{2} = 46, \text{ therefore}$$

$$a = \frac{(D - d)}{d} = \frac{46 - 24{\cdot}8}{24{\cdot}8} = 0{\cdot}8547.$$

PROBLEM 7.—When $a = 5$ grams of ammonium carbamate $NH_4CO_2NH_2$, is completely vaporised at $t = 200°$ C., it occupies a volume $v = 7{\cdot}66$ litres under a pressure P of 740 mm. of mercury. Calculate the degree of dissociation according to the equation

$$NH_4CO_2NH_2 = 2NH_3 + CO_2.$$

SOLUTION 7.—If M is the molecular weight of ammonium carbamate, a grams $= \frac{a}{M}$ gram-molecules. Let a be the degree of dissociation. Then since one molecule on dissociating gives $2a$ molecules of NH_3 and a molecules of CO_2, whilst $1 - a$ molecules of undissociated substance remain, the total number of molecules at equilibrium derived from 1 molecule of undissociated substance is $1 - a + 3a = 1 + 2a$ molecules. From $\frac{a}{M}$ molecules of undissociated substance there are, therefore, derived $\frac{a}{M}(1 + 2a)$ molecules. The equation

$$Pv = nRT,$$

therefore, becomes

$$Pv = \frac{a}{M}(1 + 2a)RT.$$

$M = 78$ and $P = \frac{740}{760}$ atmos. Substituting the numerical values we, therefore, obtain

$$\frac{740}{760} \times 7{\cdot}66 = \frac{5}{78}(1 + 2a) \times 0{\cdot}08204 \times 473,$$

$$\therefore a = \mathbf{0{\cdot}999}.$$

The compound is, therefore, completely dissociated.

Osmotic Pressure—Example

PROBLEM 8.—A solution of glucose containing $a = 36$ grams per litre gave an osmotic pressure $\pi = 4{\cdot}77$ atmospheres at $t = 25°$ C. What is the molecular weight M of glucose?

SOLUTION 8.—If a is the weight of substance in solution, and M its molecular weight, the number of dissolved molecules is $n = \frac{a}{M}$. Equation (4) therefore becomes

$$\pi v = \frac{a}{M} RT,$$

and

$$M = \frac{aRT}{\pi v}.$$

Substituting the numerical values in this equation we obtain

$$\mathbf{M} = \frac{36 \times 0{\cdot}08204 \times (273 + 25)}{4{\cdot}77 \times 1} = \mathbf{184{\cdot}5}.$$

Problems for Solution

Gas Laws

PROBLEM 9.—At 0° C. and 760 mm. pressure the volume occupied by 1 gram-molecule of oxygen is 22·4 litres. Calculate the numerical value of the gas-constant R when the units of energy are (1) the litre-atmosphere, (2) the gram-centimetre, (3) the erg, (4) the gram-calorie, (5) the joule. Given: density of mercury = 13·59, gravity-constant = 981, 1 gram-calorie = 42720 gram-centimetres = 4·183 joule.

Ans. (1) 0·08204, (2) 84720, (3) $0{\cdot}8312 \times 10^8$, (4) 1·984, (5) 8·301.

PROBLEM 10.—At 10° C. and under a pressure of 1000

grams per square centimetre, a certain mass of carbon dioxide occupies a volume of 30 cubic inches. What volume will it occupy at 20° C. and under a pressure of 850 grams per square centimetre?

Ans. 36·55 cubic inches.

PROBLEM 11.—An open vessel at a temperature of 10° C. is heated at constant pressure to 400° C. What fraction of the weight of air originally contained in the vessel is expelled?

Ans. 0·5794.

PROBLEM 12.—If the vessel in the preceding problem had been closed, and originally contained air at atmospheric pressure, what pressure would have been developed on heating to 400° C.?

Ans. 2·378 atmos.

PROBLEM 13.—From a porcelain bulb of volume 197·8 c.c. filled with air, 169·1 c.c. of air, measured at 10° C., were expelled on heating from 12° C. to t° C. The pressure throughout the experiment was 747 mm. Neglecting the expansion of the bulb, calculate t.

Ans. $t = 1772°$ C.

PROBLEM 14.—A bulb of 111·5 c.c. capacity connected with a mercury manometer was heated to 100° C. whilst open to the atmosphere. When the temperature had become constant, the atmospheric connexion was closed, and a capsule containing 0·0448 gram of acetone dropped into the heated bulb. The volume was kept constant by increasing the pressure by raising the reservoir of the manometer. The final difference of level was 16·1 cms. Calculate the molecular weight of acetone.

Ans. 57·65.

PROBLEM 15.—Half a gram of an organic compound of empirical formula CH_2O gave 327·6 c.c. of vapour at 200° C., and 750 mm. pressure. What is the molecular formula of the compound?

Ans. $C_2H_4O_2$.

PROBLEM 16.—At 17° C. 40 grams of electrolytic gas are contained in a 60 litre gas holder. What are the partial pressures of hydrogen and oxygen?

Ans. $p_{H_2} = 0·8812$ atmos., $p_{O_2} = 0·4406$ atmos.

PROBLEM 17.—The composition of air by weight is 23 per

cent. oxygen and 77 per cent. nitrogen. What are the partial pressures of oxygen and nitrogen in a vessel of 1 litre capacity which contains 2 grams of air at 15° C.?

Ans. $p_{O_2} = 0{\cdot}3397$ atmos., $p_{N_2} = 1{\cdot}299$ atmos.

PROBLEM 18.—What weights of hydrogen, oxygen, and nitrogen are contained in 10 litres, measured at 18° C. and 750 mm., of a gaseous mixture, the volumetric composition of which is $H_2 = 10$ per cent., $O_2 = 15$ per cent., $N_2 = 75$ per cent.?

Ans. $H_2 = 0{\cdot}0826$, $O_2 = 1{\cdot}985$, $N_2 = 8{\cdot}684$ grams.

Gaseous Dissociation

PROBLEM 19.—At 26° C. the vapour-density of nitrogen peroxide is 38, referred to hydrogen as unit. Calculate the proportion of N_2O_4 molecules to NO_2 molecules in the vapour at this temperature.

Ans. $N_2O_4/NO_2 = 1{\cdot}869$.

PROBLEM 20.—The vapour-density of bromine (at. wt. = 80) at 1000° C. is 76·94 (H = 1). What is the degree of dissociation of diatomic into monatomic molecules at this temperature?

Ans. 4 per cent.

PROBLEM 21.—At 70° C. and under atmospheric pressure N_2O_4 is 65·6 per cent. dissociated into NO_2. What volume will 10 grams of N_2O_4 occupy under these conditions?

Ans. 5·065 litres.

PROBLEM 22.—The vapour-density of nickel carbonyl, $Ni(CO)_4$, is 83·3 at 63° C. and 70·8 at 100° C. Calculate the percentage dissociation at these two temperatures (Ni = 58).

Ans. 0·7 per cent. and 6·66 per cent.

PROBLEM 23.—At 200° C. and atmospheric pressure the vapour-density of PCl_5 is 70 (H = 1) Calculate the degree of dissociation of the PCl_5 vapour. What are the partial pressures and concentrations in gram-molecules per litre of PCl_5, PCl_3 and Cl_2, when a gram-molecule of PCl_5 is heated under atmospheric pressure to 200° C.? (P = 31, Cl = 35·5).

Ans. Dissociation = 48·9 per cent.

Partial pressures. $PCl_5 = 0{\cdot}3431$ atmos., PCl_3 and $Cl_2 = 0{\cdot}3283$ atmos.

Concentrations. $PCl_5 = 0{\cdot}008841$, PCl_3 and $Cl_2 = 0{\cdot}008461$.

PROBLEM 24.—When ammonium carbamate, $NH_4CO_2NH_2$,

is heated, it dissociates completely into $2NH_3 + CO_2$. What volume will be occupied by the gaseous products from 7·8 grams of ammonium carbamate at 100° C. and 740 mm. pressure?

Ans. 9·428 litres.

Osmotic Pressure

PROBLEM 25.—At 10° C. the osmotic pressure of a solution of urea is 500 mm. of mercury. If the solution is diluted to 10 times its original volume, what is the osmotic pressure at 15° C. of the diluted solution?

Ans. 50·89 mm.

PROBLEM 26.—At 20° C. the osmotic pressure of a cane sugar solution is 800 mm. of mercury. What will it be at 0° C.?

Ans. 745·4 mm.

PROBLEM 27.—At 21·8° C. the osmotic pressure of a cane sugar solution containing 68·4 grams per litre was 4·81 atmos. Calculate the numerical value of the constant R when the units of pressure and volume are the atmosphere and the litre.

Ans. $R = 0·0816$.

PROBLEM 28.—The osmotic pressure of a solution of 0·184 gram of urea in 100 c.c. water was 56 cms. of mercury at 30° C. Calculate the molecular weight of urea.

Ans. 62·03.

PROBLEM 29.—What is the osmotic pressure in atmospheres at 24·2° C. of a solution of glucose containing 0·5 gram-molecule per litre?

Ans. 12·2.

PROBLEM 30. At 24° C. the osmotic pressure of a cane sugar solution is 2·51 atmos. What is the concentration of the solution in gram-molecules per litre?

Ans. 0·103.

PROBLEM 31.—At 25·1° C. the osmotic pressure of a solution of glucose containing 18 grams per litre was 2·43 atmos. Calculate the numerical value of the constant R when the unit of energy is the gram-centimetre.

Ans. $R = 84300$.

PROBLEM 32.—At 18° C. a 0·5 N – NaCl solution is 74·3 per cent. electrolytically dissociated. What would be the osmotic pressure of the solution in atmospheres at 18° C.?

Ans. 20·79.

PROBLEM 33.—A solution containing 3 gram-molecules of cane sugar per litre was found by the plasmolytic method to be isosmotic with a solution of potassium nitrate containing 1·8 gram-molecules per litre. What is the degree of dissociation of the potassium nitrate?

Ans. 0·67.

PROBLEM 34.—A solution containing 1·9 gram-molecules of calcium chloride per litre is isosmotic with a solution of glucose containing 4·05 gram-molecules per litre. What is the degree of dissociation of the calcium chloride?

Ans 0·566.

PROBLEM 35.—In a solution containing 1 gram-molecule of potassium bromide in 8 litres, the salt is 82 per cent. dissociated at 25° C. What is the osmotic pressure of the solution at this temperature?

Ans. 5·56 atmos.

CHAPTER II

DENSITY AND SPECIFIC VOLUME OF SOLIDS, LIQUIDS, LIQUID MIXTURES AND SOLUTIONS

Definitions

THE density d of a substance at a given temperature t is the weight of a given volume of it compared with the weight of the same volume of water at 4° C.; or it is the mass of unit of volume of the substance (grams per c.c.). This is usually written d_4^t.

The reciprocal of the density, the specific volume or volume of unit mass, is $V = 1/d$, and in the usual units gives the volume in c.c. occupied by one gram.

For many liquid mixtures and solutions the volume of the mixture is equal to, or approximately equal to, the sum of the volumes of the components, so that the specific volume, and, therefore, the density of the mixture may be calculated from those of its components by the mixture-formula. Conversely, the approximate composition of the mixture may be calculated from its known specific volume or density and those of its components. Thus if the specific volume of the substance A is V_A and that of the substance B is V_B, the specific volume V_M of a mixture of A and B containing p per cent. by weight of A is given by the formula

$$(1)\quad 100\ V_M = pV_A + (100 - p)\ V_B.$$

The more closely chemically related the components are, the more accurately, as a rule, does the formula reproduce the actual results.

Density and Specific Volume—Examples

PROBLEM 36.—The density of a $c = 0{\cdot}528$ molecular N-urea solution is $d = 1{\cdot}0104$. How many grams of water per gram of urea does the solution contain? What is the specific volume V of urea in the solution?

SOLUTION 36.—A c molecular N-solution contains cM gms. per litre, if M is the molecular weight of the dissolved sub-

stance ; a litre of the solution weighs 1000 d gms., and therefore contains

$$1000\,d - cM \text{ gms. of water.}$$

The c N-urea solution, therefore, contains per gm. of urea

$$\frac{1000\,d - cM}{cM}$$

$$= \frac{1000 \times 1{\cdot}0104 - 0{\cdot}528 \times 60}{0{\cdot}528 \times 60} = 30{\cdot}9 \text{ gms. of water.}$$

The specific volume V of urea in the solution is the volume in c.c. occupied by 1 gm. Now 1000 c.c. of the solution contain (1000 d − cM) gms. of water which occupies (1000 d − cM) c.c., if it is assumed that the specific volume of the water is not changed by solution. The volume occupied by cM gms. of urea is, therefore, 1000 − (1000 d − cM) c.c. Hence the specific volume is

$$V = \frac{1000 - 1000\,d + cM}{cM}$$

$$= \frac{1000 - 1010{\cdot}4 + 31{\cdot}7}{31{\cdot}7} = 0{\cdot}67 \text{ c.c. per gm.}$$

Problem 37.—What is the normality of an $a = 4$ per cent. (by weight) cane sugar solution, if the specific volume of solid cane sugar is $V = 0{\cdot}615$, and if no change of volume accompanies solution?

Solution 37.—Let the density of an a per cent. cane sugar solution = d. Then a litre of the solution weighs 1000 d gms. In these 1000 d gms. there are $\frac{a \times 1000\,d}{100} = 10 \times ad$ gms. of cane sugar. If M is the molecular weight of cane sugar the normality of the solution is $c = \frac{10 \times ad}{M}$.

d is calculated as follows: the volume of 1 litre of solution is equal to the sum of the volumes of the dissolved sugar and of the water used for its solution. A litre of solution contains $10 \times ad$ gms. of sugar, of which the volume is $10 \times adV$ c.c., and (1000 d − 10 ad) gms. of water, of which the volume is (1000 d − 10 ad) c.c. Therefore

$$1000 = 10\,adV + 1000\,d - 10\,ad$$

and

$$d = \frac{1000}{10\,a(V - 1) + 1000}.$$

The normality of the solution is, therefore,

$$c = \frac{1000\,a}{\{a(V-1)+100\}M},$$

$$= \frac{1000 \times 4}{(100 - 4 \times 0{\cdot}385)342} = \mathbf{0{\cdot}119}$$ gram-molecule per litre.

PROBLEM 38.—What is the specific volume of potassium hydroxide in a solution which contains 1 gram-molecule *of* KOH in 1000 grams of water, and of which the density is $d = 1{\cdot}052$, if the density of water is taken = 1·000, and if it is assumed that the specific volume of water is not changed by the process of solution?

SOLUTION 38.—If M is the molecular weight of KOH, then $1000 + M$ grams of the solution occupy a volume of $\frac{1000 + M}{d}$ c.c. The volume of the water used in making the solution is 1000 c.c., therefore the volume of the dissolved KOH is $\frac{1000 + M}{d} - 1000$ c.c. The specific volume of the dissolved KOH, i.e. the volume in c.c. occupied by 1 gram of KOH, is, therefore,

$$\frac{1000 + M - 1000\,d}{Md} = \frac{1000 + 56{\cdot}15 - 1052}{56{\cdot}15 \times 1{\cdot}052} = \mathbf{0{\cdot}07}$$ c.c. per gram. The smallness of this value makes it probable that the assumption, that the water does not change its volume in the process of solution, is inadmissible.

PROBLEM 39.—d_4^{20} for carbon disulphide is 1·264, and for ethyl alcohol 0·7963. What is its value for a mixture of carbon disulphide and alcohol containing 79·82 per cent. of the former?

SOLUTION 39.—Since $V = 1/d$ we may write formula (1) in the form

$$\frac{100}{d_M} = \frac{p}{d_A} + \frac{(100 - p)}{d_B}.$$

$p = 79{\cdot}82$, $d_A = 1{\cdot}264$, $d_B = 0{\cdot}7963$, therefore

$$\frac{100}{d_M} = \frac{79{\cdot}82}{1{\cdot}264} + \frac{20{\cdot}18}{0{\cdot}7963},$$

and $\mathbf{d_M = 1{\cdot}130}$. (Observed, 1·122.)

Problems for Solution

PROBLEM 40.—The density of a 2·31 per cent. solution of ammonia is 0·990. What is the concentration of the solution in gram-molecules per litre?

Ans. 1·345.

PROBLEM 41.—d_4 for a 10 per cent. NH_4Cl solution = 1·029, for solid NH_4Cl = 1·536, and for water = 0·9974. Calculate the change of volume per 100 grams solution in making a 10 per cent solution of NH_4Cl. What is the specific volume of NH_4Cl in the solution, if that of the water remains constant?

Ans. Expansion = 0·48 c.c. per 100 grams solution. Sp. vol. NH_4Cl = 0·699 c.c. per gram.

PROBLEM 42.—The density of a 4·526 per cent. solution of $HgCl_2$ in water at 16° C. = 1·038, and that of an 11·88 per cent. solution in alcohol at 16° C. = 0·8857. The density of water at 16° C. = 0·9979, and of alcohol = 0·7939. Calculate the concentration of each solution, and the specific volume of $HgCl_2$ in each. Assume no change in the specific volumes of the water and alcohol on solution.

Ans. Conc. aqueous solution = 0·1733 gram-molecule per litre. Conc. alcoholic solution = 0·3883 gram-molecule per litre.

Sp. vol. in aqueous solution = 0·1575 c.c. per gram, in alcoholic solution = 0·1635 c.c. per gram.

PROBLEM 43.—For a 5·18 per cent. solution of phenol in water d_4^{15} = 1·0042; for water d_4^{15} = 0·9991. What is the concentration of the solution in moles per litre, and in moles phenol per mole water? What is the specific volume of phenol in the solution, if the specific volume of the water is assumed to remain constant?

Ans. Conc. = 0·5534 mole per litre = 0·01046 mole phenol per mole water.

Sp. vol. = 0·9363 c.c. per gram.

PROBLEM 44.—d_4^{15} for ethyl alcohol = 0·7936, for water = 0·9991, and for a 50 per cent. solution of alcohol in water = 0·9180. What is the contraction on mixing 50 grams of alcohol with 50 grams of water at 15° C.? Assuming the specific volume of the water to remain constant, compare the

specific volume of pure alcohol with that of the alcohol in the solution.

Ans. Contraction = 4·16 c.c. Sp. vol. of pure alcohol = 1·260, of alcohol in the solution = 1·177 c.c. per gram.

PROBLEM 45.—$d_4^{18\cdot7}$ for ethylene dibromide = 2·183, for propyl alcohol = 0·8066, and for a solution of p per cent. ethylene dibromide in propyl alcohol = 0·8608. Calculate the value of p.

Ans. 10·10. (Observed, 10·01.)

PROBLEM 46 (cf. preceding problem).—Calculate the density at 18·7° C. of a 20·95 per cent. solution of ethylene dibromide in propyl alcohol.

Ans. 0·9292. (Observed, 0·9291.)

PROBLEM 47.—d_4^{20} for carbon disulphide = 1·264, for ethyl alcohol = 0·7963 and for a 50·77 per cent. solution of carbon disulphide in alcohol = x. Calculate the value of x.

Ans. 0·9804. (Observed, 0·9718.)

PROBLEM 48.—$d_4^{16\cdot3}$ for aniline = 1·025, for ethyl alcohol = 0·8081 and for a p per cent. solution of aniline in alcohol = 0·9763. Calculate p.

Ans. 81·34. (Observed, 79·24.)

PROBLEM 49.—d_4^{20} for benzene = 0·8814, for ethyl alcohol = 0·7930. What is its value for a 21·12 per cent. solution of benzene in alcohol?

Ans. 0·8104. (Observed, 0·8106.)

PROBLEM 50 (cf. preceding problem).—The density of a p per cent. solution of benzene in alcohol at 20° C. is 0·8604. What is the value of p?

Ans. 77·94. (Observed, 79·10.)

CHAPTER III

SPECIFIC AND MOLECULAR REFRACTIVITY

Definitions

THE refractive index n of a substance for light of a given wave-length, varies with the temperature, but the expressions $\frac{n-1}{d}$ (Gladstone and Dale), and $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ (Lorentz and Lorenz), where d is the density of the substance at the temperature at which n is measured, are, for a given substance, almost constant and independent of the temperature. This is especially the case with the latter expression, which remains approximately constant even for different states of aggregation of the substance (e.g. liquid and vapour). The value of $\frac{n-1}{d}$ or of $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ is called the specific refractive power or specific refractivity of the substance. If the specific refractivity is multiplied by the molecular weight M of the substance, the molecular refractivity (1) $\frac{(n-1)M}{d}$ or (2) $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$ is obtained. The molecular refractivity of a compound may be calculated from the atomic refractivities of its component elements. For monovalent elements (e.g. H_2, Cl_2, Br_2) the atomic refractivity is practically constant and independent of the nature of the other elements with which they are united. For polyvalent elements (e.g. O_2, C, N_2) the value of the atomic refractivity varies with the mode of union to the other elements of the compound, but is constant for a given mode of union. Thus in the case of carbon the atomic refractivity of a singly bound (saturated) carbon atom is different from that of a doubly or trebly linked carbon atom. This can be allowed for by assigning a definite "atomic" refractivity to an ethylene (double) and to an

acetylene (triple) bond. The molecular refractivity, as calculated from the refractive index, may, therefore, sometimes serve as a guide to the constitution of a compound. The following are the atomic refractivities for the D line (sodium light), calculated according to Lorentz and Lorenz's formula, of the elements required in the following problems. Carbon (singly bound) = 2·501, hydrogen = 1·051, oxygen in a hydroxyl (– OH) group = 1·521, oxygen in ethers = 1·683, oxygen in a carbonyl (>C = O) group = 2·287, chlorine = 5·998, ethylene bond = 1·707, acetylene bond = 2·10.

Refractivity of Mixtures

The specific refractivity of a homogeneous mixture or solution may be calculated (as a rule with close approximation to the observed value) from the specific refractivities of its components by the mixture-formula (cf. specific volume). Thus if n_A is the refractive index of substance A, n_B that of substance B and n_M that of a mixture containing p per cent. by weight of A, all for light of the same wave-length, and d_A, d_B and d_M the corresponding densities, we have, using Gladstone and Dale's formula,

$$(3)\quad \frac{n_M - 1}{d_M} = \frac{n_A - 1}{d_A} \cdot \frac{p}{100} + \frac{n_B - 1}{d_B} \cdot \frac{(100 - p)}{100},$$

or, using Lorentz and Lorenz's formula,

$$(4)\quad \frac{n^2_M - 1}{n^2_M + 2} \cdot \frac{1}{d_M} = \frac{n^2_A - 1}{n^2_A + 2} \cdot \frac{p}{100\, d_A} + \frac{n^2_B - 1}{n^2_B + 2} \cdot \frac{(100 - p)}{100\, d_B}.$$

Conversely, if the specific refractivites and densities of the mixture and its components are known, the composition of the mixture may be calculated.

Refractivity—Examples

Problem 51.—For propionic acid $d^0_4 = 1{\cdot}0158$ and n_D, the refractive index for sodium light, = 1·3953. Calculate the molecular refractivity of propionic acid by Lorentz and Lorenz's formula and compare it with the value calculated from the atomic refractivities given above.

Solution 51.—M, the molecular weight of propionic acid, = 74. Substituting the numerical values in formula (2) we obtain

$$\frac{(1{\cdot}3953)^2 - 1}{(1{\cdot}3953)^2 + 2} \times \frac{74}{1{\cdot}0158} = 17{\cdot}48$$

for the molecular refractivity.

From the atomic refractivities we obtain for

$$CH_3 \cdot CH_2 \cdot C\begin{matrix}=O\\ \diagdown OH\end{matrix}$$

3 carbon atoms = 3 × 2·501 = 7·503
6 hydrogen atoms = 6 × 1·051 = 6·306
1 hydroxylic oxygen atom = 1 × 1·521 = 1·521
1 carbonyl oxygen atom = 1 × 2·287 = 2·287

Molecular refractivity = **17·62.**

PROBLEM 52.—d_4^{20} for ether = 0·7208, for ethyl alcohol = 0·7935 and for a mixture of ether and alcohol containing p per cent. of alcohol = 0·7389. At 20° C. the refractive indices for sodium light are, for ether 1·3536, for alcohol 1·3619, and for the mixture 1·3572. Calculate the value of p, using the Gladstone and Dale formula.

SOLUTION 52.—Substituting the numerical values in equation (3) we obtain

$$\frac{(1{\cdot}3572 - 1)}{0{\cdot}7389} = \frac{(1{\cdot}3619 - 1)}{0{\cdot}7935} \cdot \frac{p}{100} + \frac{(1{\cdot}3536 - 1)}{0{\cdot}7208} \cdot \frac{(100 - p)}{100},$$

$\therefore$ **p = 20·81.** (Observed, 20·71.)

Problems for Solution

PROBLEM 53.—At 17·4° the refractive index of methyl alcohol for sodium light (n_D) = 1·3297 and its density = 0·7945. Calculate the molecular refractivity according to both (*a*) Gladstone and Dale's, and (*b*) Lorentz and Lorenz's formula, and (*c*) compare the value for the latter with that calculated from the atomic refractivities.

Ans. (*a*) 13·27, (*b*) 8·21, (*c*) 8·23.

PROBLEM 54.—$d_4^{23\cdot5}$ for liquid hydroxylamine = 1·205 and n_D = 1·4405. (*a*) Calculate the molecular refractivity (L. and L.). (*b*) What is the atomic refractivity of nitrogen in the compound?

Ans. (*a*) 7·23, (*b*) 2·556.

PROBLEM 55.—At 20° the density of chloroform = 1·4823 and the refractive index for the D line = 1·4472. Given the atomic refractivities of carbon and hydrogen, calculate that of chlorine (L. and L.).

Ans. 5·999.

PROBLEM 56.—At 20° the substance C_3H_6O has a density of 0·8005 and a refractive index for the D line of 1·3641. Using Lorentz and Lorenz's formula, determine whether it has the constitution (*a*) $CH_2 : CH \cdot CH_2OH$, or (*b*) $CH_3 \cdot CO \cdot CH_3$.

Ans. (*b*).

PROBLEM 57.—At 17·5° the density of ethyl alcohol = 0·8020, and its refractive index for the D line = 1·3619. At 17·8° the density of normal propyl alcohol = 0·8074, and its refractive index for the D line = 1·3861. From these data calculate the molecular refractivity of normal butyl alcohol according to Lorentz and Lorenz's formula.

Ans. 22·20, (Observed, 22·11).

PROBLEM 58.—For ethyl acetate $d_4^{16\cdot4} = 0{\cdot}9028$ and $n_D = 1{\cdot}3742$. (*a*) Calculate the molecular refractivity (L. and L.), and (*b*) compare it with the value calculated from the atomic refractivities.

Ans. (*a*) 22·27, (*b*) 22·38.

PROBLEM 59.—For cinnamyl alcohol $C_6H_5 . CH : CH . CH_2OH$, $d_4^{26\cdot6} = 1{\cdot}0555$ and $n_D = 1{\cdot}5763$. (*a*) Calculate the molecular refractivity (L. and L.), and (*b*) compare it with the value calculated from the atomic refractivities.

Ans. (*a*) 42·03, (*b*) 41·37.

PROBLEM 60.—At the temperature t the density of water is d_4^t and the refractive index for sodium light n_D. From these data test the constancy of the specific refractivity as calculated by Gladstone and Dale's, and Lorentz and Lorenz's formula.

t	d_4^t	n_D
20°	0·99823	1·3330
40°	0·99224	1·3307
80°	0·97183	1·3230

PROBLEM 61.—The specific refractivity (L. and L.) of glycerine for the C line = 0·2219, and of propyl alcohol = 0·2903. From these data calculate the atomic refractivity of hydroxylic oxygen for the C line.

Ans. 1·50.

PROBLEM 62.—At 18·07° the density of ethylene dibromide = 2·1830, of propyl alcohol = 0·80659, and of a mixture of the two containing p per cent. by weight of dibromide = 0·86081. At the same temperature the refractive index of

the dibromide for the D line = 1·5404, of propyl alcohol = 1·3862 and of the mixture = 1·3919. Calculate the value of p, (*a*) using the Gladstone and Dale formula, (*b*) using the Lorentz and Lorenz formula.

Ans. (*a*) 10·17, (*b*) 10·16. (Observed, 10·01.)

PROBLEM 63.—At 18·07° the density of a mixture of ethylene dibromide and propyl alcohol containing 20·95 per cent. of the former is 0·92908. From the data in the preceding problem calculate its refractive index for the D line (*a*) according to Gladstone and Dale's formula, (*b*) according to Lorentz and Lorenz's formula.

Ans. (*a*) 1·39983, (*b*) 1·39932. (Observed, 1·39913.)

PROBLEM 64.—At 20° the density of ether = 0·72078, of benzene = 0·87953, and of a mixture containing p per cent. of benzene = 0·75299. The corresponding refractive indices are (for sodium light), ether = 1·35360, benzene = 1·49996, mixture = 1·38227. Calculate the value of p by the Gladstone and Dale formula.

Ans. 21·96. (Observed, 21·06.)

PROBLEM 65.—At 18·07° the density of a 5 per cent. sodium chloride solution = 1·0345 and the refractive index (D line) = 1·3423. At the same temperature the density of water = 0·99866 and the refractive index = 1·3335. Calculate the specific refractivity of sodium chloride (Gladstone and Dale).

Ans. 0·274.

PROBLEM 66.—At 18·07° the density of a p per cent. sodium chloride solution = 1·0201 and the refractive index = 1·3388. Using the result obtained in the preceding problem, calculate the value of p (G. and D.).

Ans. 3·005. (Observed, 3·000).

PROBLEM 67.—At 21·8° the density of water = 0·9978 and of a 6·80 per cent. sodium sulphate solution = 1·0596. At the same temperature the refractive index of water for sodium light = 1·33308 and of the solution = 1·34291. Calculate the specific refractivity of sodium sulphate by the Gladstone and Dale formula.

Ans. 0·18382.

PROBLEM 68.—At 21·8° the density of a p per cent. sodium sulphate solution = 1·0782 and n_D = 1·34571. From the data in the preceding problem calculate the value of p.

Ans. 8·78. (Observed, 8·80.)

CHAPTER IV

MOLECULAR WEIGHT FROM LOWERING OF VAPOUR-PRESSURE, LOWERING OF FREEZING-POINT AND ELEVATION OF BOILING-POINT.—DEGREE OF DISSOCIATION OF ELECTROLYTES.—MOLECULAR LOWERING OF FREEZING-POINT AND ELEVATION OF BOILING-POINT FROM LATENT HEATS OF FUSION AND EVAPORATION

Molecular Weight from Lowering of Vapour-pressure

THE relative lowering of the vapour-pressure of a pure solvent by a dissolved substance is equal to the ratio of the number of molecules of dissolved substance to the number of molecules of solvent in the dilute solution (Raoult), that is,

$$(1)\quad \frac{p_0 - p}{p_0} = \frac{n}{N},$$

where p_0 is the vapour-pressure of the pure solvent, p that of the solution at the same temperature, n the number of molecules of dissolved substance, and N the number of molecules of solvent in the solution. p_0 and p must, of course, be measured in the same unit, but, since we are here dealing with a ratio, the unit chosen is immaterial.

This relation may be used as follows for the determination of the molecular weights of dissolved substances. If a is the weight of the dissolved substance, and b that of the solvent in the solution, m the molecular weight of the dissolved substance, and M that of *the solvent in the gaseous state*, then the number of molecules of dissolved substance $= \frac{a}{m}$ and the number of molecules of solvent $= \frac{b}{M}$. Therefore

$$(2)\quad \frac{p_0 - p}{p_0} = \frac{n}{N} = \frac{a/m}{b/M} = \frac{aM}{bm}.$$

Vapour-pressure and Temperature

The relation between the vapour-pressure of a liquid and the temperature is expressed by the equation (Clausius),

$$(3)\quad \frac{d \log_e p}{dT} = \frac{-L}{RT^2}.$$

p is the vapour-pressure of the liquid at the absolute temperature T, L the molecular heat of evaporation of the liquid, and R the gas-constant, the numerical value of which is 1·985 (in round numbers 2) when the gram-calorie is the unit of energy.

If we assume that L is independent of the temperature and integrate equation (3) between the temperatures T_0 and T_1, we obtain

$$(4)\quad \log_e \frac{p_0}{p_1} = \frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right) = \frac{L}{R}\left(\frac{T_1 - T_0}{T_0\, T_1}\right),$$

where p_0 and p_1 are the vapour-pressures corresponding to the absolute temperatures T_0 and T_1, or, converting the natural to common logarithms,

$$(5)\quad \log \frac{p_0}{p_1} = \log p_0 - \log p_1 = \frac{L}{2{\cdot}3R}\left(\frac{T_1 - T_0}{T_0\, T_1}\right).$$

For small intervals of temperature the assumption that L is constant will, in most cases, be practically true. For larger intervals of temperature L may be taken as the latent heat at the mean temperature $\frac{T_0 + T_1}{2}$. Since in equation (5) we are concerned only with the ratio of the vapour-pressures, p_0 and p_1 may be expressed in any unit.

Vapour-pressure—Examples

Problem 69.—What is the concentration, in gram-molecules per 1000 grams water, of an aqueous solution which at $t_0 = 100{\cdot}42°$ C. has a vapour-pressure $p = 758{\cdot}2$ mm. of mercury? The molecular heat of evaporation of water is $L = -9600$ cal.

Solution 69.—The problem can be solved by equation (1) if the vapour-pressure p_0 of water at 100·42° C. can be calculated. This can be done by equation (5) as follows: Under a pressure $p_1 = 760$ mm. of mercury (atmospheric pressure) water boils at $t_1 = 100°$ C. or $T_1 = 373°$ absolute, that is, at $T_1 = 373$ the vapour-pressure of water $= p = 760$ mm.

$T_0 = t_0 + 273 = 100{\cdot}42 + 273 = 373{\cdot}42$ and $L = -9600$. Substituting these numerical values in (5), we obtain

$$\log p_0 = \log 760 + \frac{-9600 \times -0{\cdot}42}{2{\cdot}3 \times 1{\cdot}985 \times 373 \times 374{\cdot}42} = 2{\cdot}89,$$

$$\therefore \mathbf{p_0 = 771{\cdot}2} \text{ mm.}$$

Accordingly, by (1),

$$\frac{p_0 - p}{p_0} = \frac{771{\cdot}2 - 758{\cdot}2}{771{\cdot}2} = \frac{0{\cdot}01685}{1} = \frac{n}{N}$$

The solution, therefore, contains 0·01685 gram-molecule of dissolved substance per gram-molecule of water, and, since the gram-molecule of water = 18 grams, it contains $\frac{0{\cdot}01685 \times 1000}{18} = \mathbf{0{\cdot}936}$ gram-molecule of dissolved substance per 1000 grams water.

PROBLEM 70.—Under a pressure of 760 mm. ether boils at $t_1 = 35°$ C. Its molecular heat of evaporation is − 6640 calories. (*a*) What is the vapour-pressure p_0 of ether at $t_0 = 30°$ C.? (*b*) What volume will be occupied by a litre of air at a pressure $P = 720$ mm. after being bubbled through ether at 30° C., if the total pressure be kept constant at 720 mm. during the process, and (*c*) how many (x) grams of ether will evaporate during the process?

SOLUTION 70.—(*a*) The vapour-pressure at 30° C. may be calculated from equation (5). $T_0 = t_0 + 273 = 303$. $T_1 = t_1 + 273 = 308$. $p_1 = 760$. $L = -6640$. Therefore

$$\log p_0 = \log 760 + \frac{-6640 \times 5}{2{\cdot}3 \times 1{\cdot}985 \times 303 \times 308}$$

$$\text{and } \mathbf{p_0 = 635} \text{ mm.}$$

(*b*) The volume of air, which has been bubbled through ether at 30° C. under the constant pressure $P = 720$ mm., increases until the partial pressure of the air becomes $p = P - p_0$, where p_0 is the vapour-pressure of ether at 30° C. From Boyle's law we get the final volume v assumed by 1 litre of air after being bubbled through the ether. Thus

$$\frac{v}{1} = \frac{P}{P - p_0} = \frac{720}{720 - 635} = \frac{720}{85},$$

$$\therefore \mathbf{v = 8{\cdot}5} \text{ litres.}$$

(*c*) These 8·5 litres contain ether vapour at a partial pressure $p_0 = 635$ mm. The weight x of this ether vapour is to be calculated.

According to equation (2), p. 1, (see also Problem 2),

$$p_0 v = \frac{x}{M} R T_0,$$

where M is the molecular weight of ether vapour. Hence

$$x = \frac{p_0 v M}{R T_0}.$$

If p_0 and v are expressed in atmospheres and litres the value of R is 0·08204. Therefore

$$x = \frac{\frac{635}{760} \times 8{\cdot}5 \times 74}{0{\cdot}08204 \times 303} = \mathbf{21{\cdot}15 \text{ grams.}}$$

PROBLEM 71.—The vapour-pressure of a solution containing 6·69 grams of $Ca(NO_3)_2$ in 100 grams of water is 746·9 mm. at 100° C. What is the degree of dissociation of the salt?

SOLUTION 71.—Let a be the degree of dissociation, then, since $Ca(NO_3)_2$ dissociates into 3 ions, one $Ca^{\cdot\cdot}$ and two NO'_3, one gram-molecule of $Ca(NO_3)_2$ gives on dissociation a gram-molecule of $Ca^{\cdot\cdot}$ and $2a$ gram-molecule of NO'_3, whilst $(1 - a)$ gram-molecule of undissociated salt remains. The total number of molecules derived from one gram-molecule of $Ca(NO_3)_2$ is, therefore, $1 - a + 3a = 1 + 2a$. From 6·69 grams $= \frac{6{\cdot}69}{164{\cdot}1}$ gram-molecules of $Ca(NO_3)_2$ there are, therefore, derived

$$n = \frac{6{\cdot}69}{164{\cdot}1}(1 + 2a) \text{ gram-molecules,}$$

164·1 being the molecular weight of $Ca(NO_3)_2$.

According to (1)

$$\frac{p_0 - p}{p_0} = \frac{n}{N}.$$

$p = 746{\cdot}9$ mm. and p_0 for pure water at 100° = 760 mm. N = weight of water in the solution divided by the molecular weight of water as vapour $= \frac{100}{18}$. Hence

$$\frac{760 - 746{\cdot}9}{760} = \frac{6{\cdot}69}{164{\cdot}1}(1 + 2a) \times \frac{18}{100},$$

$$\therefore a = \mathbf{0{\cdot}675}.$$

Lowering of Freezing-point

If t° is the freezing-point of a pure solvent, and t_1° that of a solution containing c gram-molecules of dissolved substance per 1000 grams of solvent, the lowering of the freezing-point $\Delta = t - t_1$ is proportional to c, that is, the lowering of the freezing-point of a pure solvent by a dissolved substance is proportional to the concentration of the latter, or

$$(6)\quad \Delta = Kc.$$

The value of the constant K depends only on the solvent, and on the unit of concentration chosen. We shall take as our unit concentration, one gram-molecule of solute in 1000 grams of solvent. If in (6) we put $c = 1$, we obtain $\Delta = K$. K is, therefore, the lowering of the freezing-point of the solvent caused by dissolving 1 gram-molecule of a normal (non-dissociating and non-associating) solute in 1000 grams of solvent. It is called the molecular lowering of the freezing-point.

(Two other units of concentration are often used, namely, (1) one gram-molecule of solute in 100 grams of solvent, and (2) one gram-molecule of solute in 1 gram of solvent. If K' is the molecular lowering in the first case, and K'' that in the second case, the relation between K, K' and K'' is $K' = 10\ K$, $K'' = 1000\ K$.)

If the solution contains a grams of solute in b grams of solvent, and if M is the molecular weight of the solute, the concentration of the solute is $\frac{a}{M}$ gram-molecules in b grams of solvent, or $\frac{1000\ a}{Mb}$ gram-molecules per 1000 grams solvent. Therefore, from (6),

$$(7)\quad \Delta = K \cdot \frac{1000\ a}{Mb}.$$

By various transformations of this equation any of the quantities may be calculated if the others are known. In (7), $\frac{1000\ a}{b}$ is the weight of solute in 1000 grams of solvent. If we put this $= W$, the equation becomes

$$(8)\quad \Delta = K\frac{W}{M} \text{ or } \frac{\Delta}{K} = \frac{W}{M},$$

a form which is particularly clear and easy of application.

The constant K for a given solvent may be found empirically by (6), (7) or (8), by observing the depressions of the freezing-point of the pure solvent caused by known concentrations of substances of which the molecular weights are known, and taking the mean value; or it may be calculated from the latent heat of fusion of the solvent by means of the relation (van't Hoff)

$$(9)\quad K = \frac{RT^2}{1000l}.$$

T ($= 273 + t$) is the freezing-point of the pure solvent on the absolute scale, l the latent heat of fusion of 1 gram of the solvent in calories and R the gas-constant (1·985, or, in round numbers, 2).

(If the constants K' or K'' as defined above are used, then

$$K' = \frac{RT^2}{100\,l} \text{ and } K'' = \frac{RT^2}{l}.)$$

Elevation of Boiling-point

For the elevation of the boiling-point of a pure solvent by a dissolved substance equations exactly analogous to (6), (7), (8) and (9) hold. In this case, however, Δ is the elevation of the boiling-point and is equal to $t_1 - t$, where t is the boiling-point of the pure solvent and t_1 that of a solution containing c gram-molecules of solute of molecular weight M per 1000 grams of solvent, or a grams of solute in b grams of solvent, or W grams of solute in 1000 grams of solvent. K is the molecular elevation of the boiling-point, caused by dissolving one gram-molecule of a normal solute in 1000 grams of solvent. In equation (9) T ($= 273 + t$) is the boiling-point of the pure solvent on the absolute scale and l is the latent heat of evaporation of one gram of solvent in calories.

(As in the case of the freezing-point, K' and K'' are the molecular elevations of the boiling-point when either of the other common units of concentration are used. Their relations to K and l are the same as those given under the freezing-point.)

Freezing-point—Examples

PROBLEM 72.—The freezing-point of a solution of 0·684 gram of cane sugar in 100 grams of water is – 0·037° C.,

and that of a solution of 0·585 gram of sodium chloride in 100 grams of water is – 0·342° C. Calculate the molecular lowering of the freezing-point for water, the apparent molecular weight of the sodium chloride and its degree of dissociation.

SOLUTION 72.—From equation (7) we obtain

$$K = \frac{\Delta M b}{1000\, a}.$$

In the case of the cane sugar solution $\Delta = 0{\cdot}037$, $M = 342$, $a = 0{\cdot}684$, $b = 100$, therefore,

$$\mathbf{K} = \frac{0{\cdot}037 \times 342 \times 100}{1000 \times 0{\cdot}684} = \mathbf{1{\cdot}85}.$$

If M' is the apparent molecular weight of the sodium chloride, we obtain from (7)

$$M' = K\frac{1000a}{\Delta b}.$$

In this case $K = 1{\cdot}85$, $a = 0{\cdot}585$, $b = 100$, $\Delta = 0{\cdot}342$, therefore,

$$\mathbf{M'} = \frac{1{\cdot}85 \times 1000 \times 0{\cdot}585}{0{\cdot}342 \times 100} = \mathbf{31{\cdot}65}.$$

Let the degree of dissociation of the sodium chloride be α, that is, of 100 molecules of sodium chloride let 100 α be dissociated into the ions Na' and Cl', and, therefore, 100 $(1 - \alpha)$ undissociated. The total number of molecules produced from 100 molecules of NaCl is, therefore,

$$100(1 - \alpha) + 2 \times 100\,\alpha = 100(1 + \alpha).$$

If $M_1 = 58{\cdot}5$ is the molecular weight of sodium chloride, the solution containing 0·585 gram in 100 grams of water would contain, if the sodium chloride were undissociated, $\frac{0{\cdot}585 \times 1000}{M_1 \times 100} = \frac{5{\cdot}85}{M_1}$ gram-molecules in 1000 grams of water. If the degree of dissociation is α, the solution contains $\frac{5{\cdot}85}{M_1}(1 + \alpha)$ gram-molecules in 1000 grams of water.

From (6), therefore,

$$\Delta = Kc$$

$$0{\cdot}342 = 1{\cdot}85 \times \frac{5{\cdot}85}{M_1}(1 + \alpha) = 1{\cdot}85 \times \frac{5{\cdot}85}{58{\cdot}5}(1 + \alpha)$$

$$\therefore \alpha = \mathbf{0{\cdot}85}.$$

Or, the apparent molecular weight of NaCl in the solution is

$$M' = \frac{\text{weight of NaCl dissolved in 1000 grams water}}{\text{number of dissolved molecules in 1000 grams water}}$$

$$= \frac{5{\cdot}85}{\frac{5{\cdot}85}{M_1}(1+\alpha)} = \frac{M_1}{1+\alpha}.$$

Hence

$$\alpha = \frac{M_1 - M'}{M'} = \frac{58{\cdot}5 - 31{\cdot}65}{31{\cdot}65} = 0{\cdot}85.$$

The salt is, therefore, 85 per cent. dissociated in the solution.

PROBLEM 73.—The latent heat of fusion of ice is $l = 80$ calories per gram. What is the molecular lowering of the freezing-point for water?

SOLUTION 73.—The freezing-point of water is 0° C. = 273° absolute. Applying equation (9), we, therefore, obtain

$$K = \frac{RT^2}{1000\,l} = \frac{1{\cdot}985 \times (273)^2}{1000 \times 80} = 1{\cdot}85.$$

Boiling-point—Examples

PROBLEM 74.—Under a pressure of 760 mm. ether boils at $t = 35°$ C. By dissolving $a = 12{\cdot}8$ grams of naphthalene in $b = 100$ grams of ether, the boiling-point of the ether is raised by $\Delta = 2{\cdot}1°$ C. Assuming that naphthalene has a normal molecular weight in ether, calculate l, the latent heat of evaporation of ether per gram, and L, the molecular heat of evaporation.

SOLUTION 74.—According to (9)

$$(1) \quad l = \frac{RT^2}{1000\,K},$$

where T is the absolute boiling-point of ether, $= 273 + t = 308$, and K the molecular elevation of the boiling-point for ether.

The latter may be calculated from the data given for the naphthalene solution. The solution contains 12·8 grams naphthalene in 100 grams ether, or $W = 128$ grams naphthalene in 1000 grams ether.

According to (8)

$$\frac{K}{\Delta} = \frac{M}{W} \text{ or } K = \frac{M\Delta}{W}.$$

The normal molecular weight M of naphthalene, $C_{10}H_8$, = 128,

$$\therefore K = \frac{128 \times 2{\cdot}1}{128} = 2{\cdot}1.$$

Substituting this value of K in (1) we obtain

$$l = \frac{1{\cdot}985 \times (308)^2}{1000 \times 2{\cdot}1} = 89{\cdot}7 \text{ calories.}$$

Since the molecular weight of ether is 74, the molecular heat of evaporation is

$$L = 89{\cdot}7 \times 74 = 6638 \text{ calories.}$$

PROBLEM 75.—A solution of barium nitrate containing $a = 11{\cdot}07$ grams in 100 grams of water boils at 100·466° C. What is the degree of dissociation of the salt? K for water $= 0{\cdot}52$.

SOLUTION 75.—The solution contains $10\,a$ grams barium nitrate per 1000 grams water. If M ($= 261{\cdot}5$) is the molecular weight of barium nitrate, it would, therefore, contain $\frac{10\,a}{M}$ gram-molecules in 1000 grams water if the salt were undissociated. Let α be the degree of dissociation. Since $Ba(NO_3)_2$ dissociates into 3 ions we obtain, exactly as in Problem 71, for the total number of gram-molecules in 1000 grams of water

$$c = \frac{10\,a}{M}(1 + 2\,\alpha).$$

Putting this value of c into equation (6) we obtain

$$\Delta = K.\frac{10\,a}{M}(1 + 2\,\alpha),$$

and, substituting the numerical values,

$$0{\cdot}466 = \frac{0{\cdot}52 \times 10 \times 11{\cdot}07}{261{\cdot}5}(1 + 2\,\alpha)$$

$$\therefore \alpha = 0{\cdot}558.$$

Problems for Solution

Vapour-pressure

PROBLEM 76.—The vapour-pressure of ether at 20° C. is 442 mm. and that of a solution of 6·1 grams of benzoic acid in 50 grams of ether is 410 mm. at the same temperature. Calculate the molecular weight of benzoic acid in ether.

Ans. 124.

PROBLEM 77.—At 10° C. the vapour-pressure of ether is 291·8 mm. and that of a solution containing 5·3 grams of benzaldehyde in 50 grams of ether is 271·8 mm. What is the molecular weight of benzaldehyde?

Ans. 114·4.

PROBLEM 78.—The vapour-pressure of alcohol at 70° C. is 540·9 mm., and at 80° C. it is 811·8 mm. Calculate the latent heat of evaporation per gram of alcohol.

Ans.—212 calories.

PROBLEM 79.—Under a pressure of 760 mm. ether boils at 35° C. A solution of 10·44 grams of aniline in 100 grams of ether has a vapour-pressure of 333 mm. at 15·3° C. The latent heat of evaporation of ether is – 89·73 calories per gram. Calculate the molecular weight of aniline in the solution.

Ans. 97·6.

PROBLEM 80.—At 0° C. the vapour-pressure of water is 4·620 mm. and of a solution of 8·49 grams of $NaNO_3$ in 100 grams of water 4·483 mm. Calculate the degree of dissociation of the $NaNO_3$.

Ans. 0·649.

PROBLEM 81.—At 25° C. the vapour-pressure of water is 23·55 mm. What is the vapour-pressure of a solution containing 6 grams of urea in 100 grams of water at the same temperature?

Ans. 23·13 mm.

PROBLEM 82.—At 0° C. the vapour-pressure of water = 4·620 mm. and that of a solution containing 21·24 grams of glycerol in 100 grams of water = 4·432 mm. Calculate the molecular weight of glycerol in the solution.

Ans. 93·9.

PROBLEM 83.—The vapour-pressure of a solution of 8·89 grams of dextrose in 100 grams of water is 4·582 mm. at 0° C., whilst that of pure water at the same temperature is 4·620 mm. Calculate the molecular weight of dextrose.

Ans. 194·5.

PROBLEM 84.—A solution containing 9·21 grams of mercuric cyanide in 100 grams of water has a vapour-pressure of 755·2 mm. at 100° C. What is the molecular weight of the

salt? What conclusion may be drawn as to the dissociation of mercuric cyanide in aqueous solution?

Ans. 262·5.

PROBLEM 85.—The vapour-pressure of a solution containing 11·94 grams of glycocoll ($C_2H_5NO_2$) in 100 grams of water is 740·9 mm. at 100° C. What is the molecular weight of the solute?

Ans. 85·5.

PROBLEM 86.—Under what pressure does water boil at a temperature of 95° C.? The latent heat of evaporation of water is – 536 calories per gram.

Ans. 636·5 mm.

PROBLEM 87.—At 0° C. the vapour-pressure of water = 4·620 mm. and that of a solution of 2·21 grams of $CaCl_2$ in 100 grams of water = 4·585 mm. Calculate the apparent molecular weight and the degree of dissociation of the $CaCl_2$.

Ans. $M = 52·5$, $\alpha = 0·557$.

PROBLEM 88.—A current of dry air was bubbled through a bulb containing a solution of 13·33 grams of urea in 100 grams of water, then through a bulb, at the same temperature, containing pure water and finally through a tube containing pumice moistened with strong sulphuric acid. The loss of weight of the water bulb = 0·0870 grams and the gain of weight of the sulphuric acid tube = 2·036 grams. Calculate the molecular weight of urea in the solution.

Ans. 56·2.

PROBLEM 89.—A current of dry air was passed first through a series of bulbs containing a solution of 8·914 grams of nitrobenzene in 100 grams of alcohol, and then through a series of bulbs containing pure alcohol. The temperature was 11° C. After the passage of the air the decrease in the weight of the bulbs containing the solution was 2·0340 grams and of the bulbs containing the pure solvent 0·0685 gram. Calculate the molecular weight of nitrobenzene in the solution.

Ans. 125·8.

PROBLEM 90 (cf. preceding problem).—In a similar experiment with ethyl benzoate the solution contained 7·394 grams of ethyl benzoate in 100 grams of alcohol. The loss of weight of the solution was 2·1585 grams and of the pure

solvent 0·0515 gram. Calculate the molecular weight of ethyl benzoate.

Ans. 146.

PROBLEM 91.—The vapour-pressure of boron trichloride is 562·9 mm. at 10° C. and 807·5 mm. at 20° C. What is the molecular heat of evaporation of boron trichloride and its boiling-point under atmospheric pressure?

Ans. $L = -5936$ cals., B.P. = 18·4° C.

Freezing-point

PROBLEM 92.—The freezing-point of pure benzene = 5·440° and that of a solution containing 2·093 grams of benzaldehyde in 100 grams of benzene = 4·440°. Calculate the molecular weight of benzaldehyde in the solution. K for benzene = 5.

Ans. 104·6.

PROBLEM 93.—A solution of 0·502 gram of acetone in 100 grams of glacial acetic acid gave a depression of the freezing-point of 0·339°. Calculate the molecular depression for glacial acetic acid.

Ans. $K = 3·9$.

PROBLEM 94.—17·79 grams of an aqueous solution containing 0·1834 gram of hydrogen peroxide gave a freezing-point of − 0·571°. What is the molecular weight of hydrogen peroxide in the solution? K for water = 1·86.

Ans. 33·9.

PROBLEM 95.—By dissolving 0·0821 gram of *m*-hydroxybenzaldehyde ($C_7H_6O_2$) in 20 grams of naphthalene (melting-point 80·1°) the freezing-point is lowered by 0·232°. Assuming that the molecular weight of the solute is normal in the solution, calculate the molecular depression for naphthalene and the latent heat of fusion per gram.

Ans. $K = 6·896$, $l = 36·2$ cals.

PROBLEM 96.—A solution of 1 gram of silver nitrate in 50 grams of water freezes at − 0·348° C. Calculate to what extent the salt is ionised in the solution. K for water = 1·86.

Ans. $\alpha = 0·59$.

PROBLEM 97.—The weights a of methyl alcohol dissolved

in 15 grams of benzene gave the depressions of the freezing-point Δ.

a	0·0478	0·0988	0·2700	0·4291	0·6636	1·093
Δ	0·360°	0·612°	1·265°	1·610°	1·978°	2·475°.

The molecular lowering of the freezing-point for benzene is $K = 5·0$. What conclusions as to the molecular condition of methyl alcohol in benzene solution may be drawn from these figures?

PROBLEM 98.—An aqueous solution of ethyl alcohol containing 8·74 grams alcohol per 1000 grams water gave a freezing-point of −0·354°. Find the molecular weight of alcohol in this solution. K for water = 1·86.

Ans. 45·9.

PROBLEM 99.—A solution of NaCl containing 3·668 grams per 1000 grams water freezes at −0·2207°. Calculate the degree of dissociation of the salt. ($K = 1·86$.)

Ans. $a = 0·892$.

PROBLEM 100.—0·2274 gram of naphthalene in 10 grams of p-toluidine (melting-point = 42·1°) caused a lowering of the freezing-point = 0·940°. Calculate the freezing-point constant and latent heat of fusion of p-toluidine.

Ans. $K = 5·29$, $l = 37·5$ cals.

PROBLEM 101.—The lowering of the freezing-point Δ was caused by dissolving a grams of formanilide in 10 grams of benzene. ($K = 5·0$.)

a	0·1255	0·3815	0·7439	1·197
Δ	0·420	0·920	1·360	1·747

What conclusions as to the state of the dissolved substance and its variation with concentration may be drawn from these figures?

PROBLEM 102.—A solution of 0·4180 gram KOH in 1000 grams water gave a freezing-point of −0·0275°, and a solution of 1·780 gram in 1000 grams water a freezing-point of −0·1147°. Calculate the degree of dissociation of the KOH in these solutions, taking $K = 1·86$.

Ans. 98·1 per cent. and 94 per cent.

PROBLEM 103.—The melting-point of phenol is 40° C. A solution containing 0·172 gram acetanilide (C_8H_9ON) in 12·54 grams phenol freezes at 39·25° C. Assuming that

acetanilide has its normal molecular weight in phenol, calculate the freezing-point constant and the latent heat of fusion of phenol.

Ans. $K = 7{\cdot}38$, $l = 26{\cdot}5$ cals.

PROBLEM 104.—A solution of 8·535 grams $NaNO_3$ in 100 grams water freezes at − 3·04° C. Calculate the degree of dissociation of the $NaNO_3$. $K = 1{\cdot}86$.

Ans. 0·629.

PROBLEM 105.—The freezing-point of a solution containing 0·510 gram-molecule of strontium formate in 1000 grams water is − 2·390°. Calculate the degree of dissociation of the salt. $K = 1{\cdot}86$.

Ans. 0·76.

PROBLEM 106.—The freezing-point of a solution of barium hydroxide containing 1 gram-molecule in 64 litres is − 0·0833°. What is the concentration of hydroxyl-ions in the solution? Take $K = 1{\cdot}89$ for concentrations in gram-molecules per litre.

Ans. 0·0284 gram-ion per litre.

PROBLEM 107.—A solution containing 2·423 grams sulphur in 100 grams naphthalene (melting-point = 80·1°) gave a lowering of the freezing-point of 0·641°, and a solution containing 2·192 grams iodine in 100 grams naphthalene a depression of 0·595°. The latent heat of fusion of naphthalene is 35·7 calories per gram. What is the molecular formula of sulphur and iodine respectively in naphthalene solution?

Ans. M for S = 264, $\therefore$ S_8, M for I = 257, $\therefore$ I_2.

PROBLEM 108.—A solution containing 0·063 gram-molecule of calcium formate in 1000 grams water freezes at − 0·316°. What is the degree of dissociation? $K = 1{\cdot}86$.

Ans. 0·85.

PROBLEM 109.—A solution containing 0·02 gram-molecule of zinc chloride per litre freezes at − 0·1035°. Calculate the degree of dissociation. $K = 1{\cdot}89$.

Ans. 0·87.

PROBLEM 110.—A solution of zinc nitrate containing 0·065 gram-molecule per litre freezes at − 0·322°. What is the concentration of the zinc ions in the solution? $K = 1{\cdot}89$.

Ans. 0·0526 gram-ion per litre.

PROBLEM 111.—The melting-point of pure copper is 1084° C. A solution of Cu_2O in copper, containing 1·16 per cent. by weight of Cu_2O freezes at 1076° C. Assuming that the molecular weight of Cu_2O in the solution corresponds to its formula, calculate the latent heat of fusion of copper per gram.

Ans. 38 cals.

PROBLEM 112.—A solution of lithium chloride containing 4·13 grams per litre freezes at − 0·343°. What is the degree of dissociation? $K = 1·89$.

Ans. 0·865.

PROBLEM 113.—The melting-point of tin = 231·611° C. and its latent heat of fusion = 14·25 calories per gram. The freezing-point of a solution containing 1·5463 grams copper in 440 grams tin is 229·692°. Calculate the molecular weight of copper in the solution.

Ans. 65·4.

PROBLEM 114.—The freezing-point of a solution containing 0·0199 gram-molecule $SrCl_2$ per litre is − 0·1015°. What is the degree of dissociation of the salt? $K = 1·89$.

Ans. 0·85.

PROBLEM 115.—A solution containing 0·834 gram Na_2SO_4 per 1000 grams water freezes at − 0·0280°. Assuming dissociation into 3 ions, calculate the degree of dissociation and the concentrations of the $Na^{\cdot}$ and SO_4'' ions. $K = 1·86$.

Ans. $\alpha = 0·782$; conc. $Na^{\cdot} = 0·0918$ gram-ion per litre; conc. $SO_4'' = 0·0459$ gram-ion per litre.

PROBLEM 116.—The vapour-pressure of water at 0° C. is 4·620 mm., and the depression of the vapour-pressure caused by dissolving 5·64 grams NaCl in 100 grams water is 0·142 mm. What is the freezing-point of this solution? $K = 1·86$.

Ans. − 3·177°.

PROBLEM 117.—The vapour-pressure of a solution containing 5·85 grams NaCl in 100 grams water is 4·460 mm. at 0° C., and that of pure water is 4·620 mm. The freezing-point of the solution is − 3·424°. Compare the degrees of dissociation obtained (1) by the vapour-pressure method, and (2) by the freezing-point method. $K = 1·86$.

Ans. (1) 0·924, (2) 0·841.

PROBLEM 118.—When mercuric cyanide, $Hg(CN)_2$, is dissolved in potassium cyanide solutions, the complex anion $Hg(CN)_{m+2}$ is formed according to the equation

$$Hg(CN)_2 + mCN' = Hg(CN)_{m+2}.$$

The freezing-point of a solution containing 0·1965 gram-molecule of KCN per litre is − 0·704°, and that of the same solution, after the addition of 0·095 gram-molecule of $Hg(CN)_2$ per litre, is − 0·530°. What is the value of m? K = 1·86. As m must be a whole number, give the nearest whole number.

Ans. m = 1·985, ∴ 2.

PROBLEM 119.—The freezing-point of a solution containing 0·01052 gram-molecule Na_2SiO_3 in 1000 grams water is − 0·0676°. Show that the salt is largely hydrolysed according to the equation

$$Na_2SiO_3 + H_2O = 2\ NaOH + SiO_2\ (colloidal).$$

PROBLEM 120.—The freezing-point of a 0·25 N-KCN solution is − 0·860°. The freezing-point of the same solution with the addition of 0·25 gram-molecule of AgCN per litre is − 0·830°. The solution of AgCN in KCN takes place according to the equation

$$m\ CN' + AgCN = (AgCN)(CN')_m.$$

What is the value of m (nearest whole number)? $K = 1·86$.

Ans. m = 1·06, ∴ 1.

Boiling-point

PROBLEM 121.—A solution containing 0·5042 gram of a substance dissolved in 42·02 grams of benzene boils at 80·175°. Find the molecular weight of the solute, having given that the boiling-point of benzene is 80.000°, and its latent heat of evaporation of 94 calories per gram.

Ans. 181·9.

PROBLEM 122.—A solution containing 0·7269 gram camphor (mol. wt. = 152) in 32·08 grams of acetone (boiling-point = 56·30° C.) boiled at 56·55° C. What is the molecular elevation for acetone and the latent heat of evaporation?

Ans. $K = 1·674$, $l = 129·5$ cals. per gram.

PROBLEM 123.—The latent heat of evaporation of carbon disulphide (boiling-point = 46·20° C.) is 85·9 cals. per gram.

The weights a of benzoic acid dissolved in 50·09 grams of CS_2 gave the elevations Δ of the boiling-point of CS_2. What is the molecular condition of benzoic acid in CS_2, and how does it vary with concentration?

a	0·9378	1·6429	2·5792	4·5519 grams.
Δ	0·187°	0·319°	0·479°	0·789°.

PROBLEM 124.—A solution of 9·472 grams CdI_2 in 44·69 grams water boiled at 100·303°. The latent heat of evaporation of water is 536 cals. per gram. What is the molecular weight of CdI_2 in the solution? What conclusion as to the state of CdI_2 in solution may be drawn from the result?

Ans. $M = 363·2$.

PROBLEM 125.—The boiling-point of a solution of 0·4388 gram NaCl in 100 grams water is 100·074° C. Calculate the apparent molecular weight of the NaCl and its degree of dissociation. $K = 0·52$.

Ans. $M = 30·84$, $\alpha = 0·897$.

PROBLEM 126.—The boiling-point of acetic acid is 118·100° and its latent heat of evaporation 121 cals. per gram. A solution containing 0·4344 gram of anthracene in 44·16 grams of acetic acid boils at 118·240°. What is the molecular weight of anthracene?

Ans. 178.

PROBLEM 127.—By dissolving 3·614 grams of $CuCl_2$ in 100 grams of alcohol the boiling-point of the alcohol is raised 0·308°. For alcohol $K = 1·15$. What is the molecular weight of the solute?

Ans. 134·9.

PROBLEM 128.—The boiling-point of a solution of 3·40 grams $BaCl_2$ in 100 grams water is 100·208°. $K = 0·52$. What is the degree of dissociation of the $BaCl_2$?

Ans. 0·725.

PROBLEM 129.—At 100° the vapour pressure of a solution of 6·48 grams NH_4Cl in 100 grams water is 731·4 mm. $K = 0·52$. What is the boiling-point of the solution?

Ans. 101·086°.

CHAPTER V

SURFACE TENSION, MOLECULAR WEIGHT AND DEGREE OF ASSOCIATION OF LIQUIDS

Definitions—Example

PROBLEM 130.—In a capillary tube of radius $r = 0{\cdot}01425$ cm., pure liquid formic acid rises to a height of $h_1 = 4{\cdot}442$ cms. at $t_1 = 16{\cdot}8°$, $h_2 = 4{\cdot}205$ cms. at $t_2 = 46{\cdot}4°$ and $h_3 = 3{\cdot}90$ cms. at $t_3 = 79{\cdot}8°$. The density of formic acid is $d_1 = 1{\cdot}207$ at $16{\cdot}8°$, $d_2 = 1{\cdot}170$ at $46{\cdot}4°$ and $d_3 = 1{\cdot}129$ at $79{\cdot}8°$. What is the molecular weight of formic acid in the liquid state, and how does it vary with temperature? ($g = 981{\cdot}1$ cms./sec.^{2}).

SOLUTION 130.—The surface tension of a liquid of density d, as determined by the height h to which it rises in a capillary tube of radius r, is

$$(1)\quad \gamma = \tfrac{1}{2}\, grhd,$$

where g is the value of gravity (gravitation constant). If the quantities on the right-hand side of the equation are expressed in C.G.S. units, g in cms./sec.^{2}, r and h in cms. and d in grams per c.c., we obtain γ in dynes per cm.

If d is the density of the liquid under investigation, and M its molecular weight, its specific volume is $v = \frac{1}{d}$ and its molecular volume is Mv. The molecular surface of the liquid is, therefore, proportional to $(Mv)^{2/3}$. The product $\gamma\,(Mv)^{2/3}$ is called the molecular surface energy, and, if we use the above units, is expressed in ergs. The molecular surface energy of any liquid diminishes with rise of temperature, and Ramsay and Shields have shown that the temperature coefficient of the molecular surface energy is the same for all liquids, and that its numerical value is $2{\cdot}121$ when the surface energy is expressed in ergs. Hence

$$(2)\quad \frac{\gamma_1 (Mv_1)^{2/3} - \gamma_2 (Mv_2)^{2/3}}{t_2 - t_1} = 2{\cdot}121,$$

where γ_1, v_1 are the surface tension and specific volume at the lower temperature t_1 and γ_2, v_2 the corresponding values at the higher temperature t_2.

The molecular weight of the substance in the liquid state is not, however, necessarily the same as the normal molecular weight, or formula weight, M. This is the case with unassociated liquids only. If the molecules in the liquid condition are associated into more or less complex groups, we must, in order to make equation (2) generally applicable, multiply the normal molecular weight M by a factor x, so that xM expresses the mean molecular weight of the substance in the liquid state between the temperatures t_1 and t_2. x is called the factor of association, and in the case of unassociated liquids its value is unity. Equation (2), therefore, becomes

$$(3)\quad \frac{\gamma_1 (xMv_1)^{2/3} - \gamma_2 (xMv_2)^{2/3}}{t_2 - t_1} = 2{\cdot}121.$$

For formic acid at $t_1 = 16{\cdot}8°$ we have

$$\gamma_1 = \tfrac{1}{2}\, grh_1d_1 = 0{\cdot}5 \times 981{\cdot}1 \times 0{\cdot}01425 \times 4{\cdot}442 \times 1{\cdot}207 = 37{\cdot}47 \text{ dynes per cm.},$$

at $t_2 = 46{\cdot}4°$

$$\gamma_2 = \tfrac{1}{2}\, grh_2d_2 = 0{\cdot}5 \times 981{\cdot}1 \times 0{\cdot}01425 \times 4{\cdot}205 \times 1{\cdot}170 = 34{\cdot}42 \text{ dynes per cm.},$$

at $t_3 = 79{\cdot}8°$

$$\gamma_3 = \tfrac{1}{2}\, grh_3d_3 = 0{\cdot}5 \times 981{\cdot}1 \times 0{\cdot}01425 \times 3{\cdot}90 \times 1{\cdot}129 = 30{\cdot}80 \text{ dynes per cm.}$$

Therefore,

$$\gamma_1(Mv_1)^{2/3} = 37{\cdot}47(46/1{\cdot}207)^{2/3} = 424{\cdot}4 \text{ ergs}$$

$$\gamma_2(Mv_2)^{2/3} = 34{\cdot}42(46/1{\cdot}170)^{2/3} = 397{\cdot}7 \quad ,,$$

$$\gamma_3(Mv_3)^{2/3} = 30{\cdot}80(46/1{\cdot}129)^{2/3} = 364{\cdot}6 \quad ,,$$

Putting these values into equation (3) we obtain, between t_1 and t_2

$$\frac{x^{2/3}(424{\cdot}4 - 397{\cdot}7)}{46{\cdot}4 - 16{\cdot}8} = 2{\cdot}121,$$

$$x^{2/3} = \frac{2{\cdot}121 \times 29{\cdot}6}{26{\cdot}7} = 2{\cdot}352,$$

$$\therefore x = (2{\cdot}352)^{3/2} = \mathbf{3{\cdot}60}.$$

The mean molecular weight of formic acid between 16·8° and 46·4° is, therefore, 3·60 × 46 = **166**.

Similarly, between t_2 and t_3,

$$\frac{x^{2/3}(397{\cdot}7 - 364{\cdot}6)}{79{\cdot}8 - 46{\cdot}4} = 2{\cdot}121,$$

$$\therefore x = 3{\cdot}13,$$

and the mean molecular weight of formic acid between 46·4° and 79·8° is 3·13 × 46 = **144**.

The molecules of formic acid are, therefore, associated into complex groups in the liquid state, and the degree of association, and, therefore, the molecular weight of the complexes diminish with increase of temperature.

Problems for Solution

PROBLEM 131.—What is the factor of association of carbon disulphide, for which at 19·4° the surface tension is 33·58 dynes per cm., and the density 1·264, and at 46·1° the surface tension is 29·41 dynes per cm., and the density 1·223?

Ans. 1·07.

PROBLEM 132.—Liquid nitrogen peroxide rises to a height of 3·14 cms. at 1·6° in a capillary tube of 0·0129 cm. radius, and to a height of 2·905 cms. in the same tube at 19·8° C. The density of the peroxide is 1·486 at 1·6°, and 1·444 at 19·8°. From these data determine whether liquid nitrogen peroxide is associated at these temperatures, and if so, to what extent.

Ans. x for N_2O_4 = 1·01 ∴ formula is N_2O_4.

PROBLEM 133.—Normal butyl alcohol at the temperature $t°$ rose to a height h in a capillary tube of radius 0·01425 cms. The density of the alcohol at each temperature was d. Calculate the factor of association and the mean molecular weight between each pair of temperatures.

t	17·4°	45·7°	77·9° C.
h	4·305	4·005	3·63 cms.
d	0·8115	0·7907	0·7634.
Ans. x		1·94	1·72
xM		143·5	127·3

PROBLEM 134.—In a capillary tube of 0·03686 cms. diameter water rose at 0° C. to a height of 8·10 cms., and at

10° C. to a height of 7·96 cms. The density of water at 0° = 0·9999 and at 10° = 0·9997. What is the factor of association and the mean molecular weight of liquid water between 0° and 10°?

Ans. $x = 3{\cdot}81$, $xM = 68{\cdot}6$.

PROBLEM 135.—In a capillary tube of radius 0·0129 cms. ethyl iodide rose to the height h at the temperature t, at which the density is d,

t	h	d
19·1°	2·445 cms.	1·937
46·2°	2·22 cms.	1·875.

What is the factor of association and mean molecular weight of ethyl iodide between these two temperatures?

Ans. $x = 1{\cdot}01$. Molecular weight ∴ normal.

CHAPTER VI

THERMOCHEMISTRY

Hess's Law

THE heat effect of a chemical reaction, for a given quantity of the reacting substances and for a definite temperature, is dependent only on the initial and final states of the reacting system. It is the same whether the reaction takes place in one or in several stages, provided that the initial and final states are the same (Hess's Law). By means of this law we are enabled to calculate the heat effect of a reaction which, for various reasons, cannot be measured directly. The reaction in question is considered as the sum or difference of others which have been measured. By suitable manipulation of the thermochemical equations all undesired substances are eliminated, and only the equation for the required reaction is left.

By the union of 12 grams of solid carbon with 32 grams of gaseous oxygen at 18° C. to form 44 grams of gaseous carbon dioxide, there is a heat evolution of 96960 calories, or, the energy-content of the system in its initial state (12 grams carbon + 32 grams oxygen) is greater than the energy-content of the system in its final state (44 grams carbon dioxide) by 96960 calories. This statement is conveniently expressed by the equation

$$C + O_2 = CO_2 + 96960 \text{ cals.}$$

The symbols in such thermochemical equations stand for definite, though unknown, amounts of energy associated with the formula-weight in grams of each substance. A knowledge of the absolute amount of energy associated with each gram-molecule is, however, unnecessary, since it is only with differences in energy that we are concerned.

Heat of Reaction at Constant Volume and Constant Pressure

The difference in energy-content between the initial and final states of the system is equal to the heat-evolution or absorption only when no external work is done during the reaction. This is the case when only solids and liquids are involved in the reaction, since in such cases the volume changes during the reaction are negligible. When gases are involved in the reaction, however, the heat of the reaction at constant pressure may differ considerably from that at constant volume, since, in the formation or absorption of one gram-molecule of a gas at T° absolute, external work equivalent to $RT = 2T$ calories is done by or on the system, and the total energy-difference between the initial and final states of the system is equal to the heat evolved + the external work done by the system.

If Q_v is the heat of the reaction in calories at constant volume (no external work condition), and Q_p that at constant pressure (external work condition), then

$$\begin{aligned} Q_v &= Q_p + nRT \\ &= Q_p + 2nT \text{ calories,} \end{aligned}$$

where n is the number of gas-molecules in the final state (on the right-hand side of the equation representing the reaction) in excess of the number in the initial state (on the left-hand side of the equation), and T the absolute temperature at which the reaction takes place.

The heat of formation of a compound is the heat evolved in the formation of a gram-molecule of the compound from its component elements.

As may be readily seen from Hess's law, the heat evolved in a chemical reaction is equal to the sum of the heats of formation of the final substances minus the sum of the heats of formation of the original substances, the heats of formation of the elements themselves being taken as zero.

In the following problems the symbol Aq denotes a large quantity of water. For example,

$$\text{NaCl} + \text{Aq} = \text{NaCl Aq}$$

means the solution of 1 gram-molecule of NaCl in much water to form a dilute solution.

Thermochemistry—Examples

PROBLEM 136.—The heat of combustion of ethyl alcohol is $Q_1 = 341800$ cals.; the heats of formation of carbon dioxide and water are $Q_2 = 96000$ cals. and $Q_3 = 68000$ cals. respectively, all at constant pressure. What is the heat of formation Q_x of ethyl alcohol?

SOLUTION 136.—The combustion of ethyl alcohol takes place according to the equation

$$(1)\quad C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O + Q_1 \text{ cals.}$$

The combustion can be regarded as taking place in 3 stages, (*a*) in the decomposition of the alcohol into its elements according to the equation

$$(2)\quad C_2H_5OH = 2C + 3H_2 + O - Q_x \text{ cals.},$$

and (*b*) and (*c*) in the combustion of 2C and $3H_2$ according to the equations

$$(3)\quad 2C + 2O_2 = 2CO_2 + 2Q_2$$

and

$$(4)\quad 3H_2 + 1\tfrac{1}{2}O_2 = 3H_2O + 3Q_3.$$

By adding (2), (3) and (4) we obtain

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O - Q_x + 2Q_2 + 3Q_3.$$

From a comparison of this equation with (1) it follows that

$$Q_1 = -Q_x + 2Q_2 + 3Q_3,$$

and, therefore,

$$\begin{aligned} Q_x &= 2Q_2 + 3Q_3 - Q_1 \\ &= 192000 + 204000 - 341800 = \mathbf{54200} \text{ cals.} \end{aligned}$$

PROBLEM 137.—By the solution of $a = 10$ grams of metallic sodium in much water $q_1 = 18800$ cals. are liberated, and by the solution of $b = 20$ grams of sodium oxide under the same conditions $q_2 = 20400$ cals. are liberated. What is the molecular heat of formation Q_x of Na_2O, if the molecular heat of formation of liquid water from gaseous oxygen and hydrogen is $Q_3 = 68000$ cals.?

SOLUTION 137.—The solution of 1 gram-atom of metallic Na in water takes place according to the thermochemical equation

$$(1)\quad Na + H_2O = NaOH + \tfrac{1}{2}H_2 + Q_1,$$

and the solution of 1 gram-molecule of Na_2O according to the equation

$$(2)\ Na_2O + H_2O = 2NaOH + Q_2.$$

By multiplying equation (1) by 2 and subtracting equation (2) we obtain

$$(3)\ 2Na + H_2O = Na_2O + H_2 + 2Q_1 - Q_2.$$

To obtain the heat of formation of Na_2O we must add to equation (3) the equation representing the formation of a gram-molecule of liquid water from gaseous hydrogen and oxygen, namely :—

$$(4)\ H_2 + \tfrac{1}{2}O_2 = H_2O + Q_3.$$

From (3) and (4) we thus get

$$2Na + \tfrac{1}{2}O_2 = Na_2O + 2Q_1 - Q_2 + Q_3.$$

The required heat of formation of Na_2O is therefore

$$(5)\ Q_x = 2Q_1 + Q_3 - Q_2.$$

If M is the atomic weight of Na and M' the molecular weight of Na_2O, then

$$Q_1 = \frac{q_1 M}{a} \text{ and } Q_2 = \frac{q_2 M'}{b},$$

or, putting in the numerical values,

$$Q_1 = \frac{18800 \times 23}{10} = 43200 \text{ cals.},$$

and

$$Q_2 = \frac{20400 \times 62}{20} = 63200 \text{ cals.}$$

Accordingly, from (5),

$$Q_x = 2 \times 43200 + 68000 - 63200 = \mathbf{91200} \text{ cals.}$$

Problem 138.—Auric hydroxide dissolves in hydrochloric acid according to the thermochemical equation

$$Au(OH)_3 + 4HCl = HAuCl_4 + 3H_2O + 23000 \text{ cals.},$$

and in hydrobromic acid according to the corresponding equation

$$Au(OH)_3 + 4HBr = HAuBr_4 + 3H_2O + 36800 \text{ cals.}$$

On mixing 1 gram-molecule $HAuBr_4$ with 4 gram-molecules HCl there is a heat absorption of 510 cals. What percentage of the bromoauric acid has been transformed into chloroauric acid in the process?

SOLUTION 138.—The ratio of the quantity x of bromoauric acid transformed into chloroauric acid to the total quantity of bromoauric acid employed is equal to the ratio of the observed heat evolution to the molecular heat of the reaction

$$HAuBr_4 + 4HCl = HAuCl_4 + 4HBr.$$

The molecular heat of this reaction is obtained by subtracting equation (2) from equation (1), giving equation (3).

(1) $Au(OH)_3 + 4HCl = HAuCl_4 + 3H_2O + 23000$ cals.
(2) $Au(OH)_3 + 4HBr = HAuBr_4 + 3H_2O + 36800$ cals.
(3) $HAuBr_4 + 4HCl = HAuCl_4 + 4HBr - 13800$ cals.

For the quantity x (per cent.) transformed we therefore get

$$\frac{x}{100} = \frac{-510}{-13800},$$

$$x = 3{\cdot}7 \text{ per cent.}$$

Problems for Solution

PROBLEM 139.—At 17° C. the heat of combustion of carbon to carbon dioxide is 96960 cals., and that of carbon monoxide to carbon dioxide 67960 cals., both at constant pressure. What is the heat of formation of carbon monoxide (*a*) at constant pressure, (*b*) at constant volume?

Ans. (*a*) 29000 cals., (*b*) 29290 cals.

PROBLEM 140.—By the combustion at constant pressure of 2 grams of hydrogen with oxygen to form liquid water at 17° C. 68360 cals. are evolved. What is the heat evolution at constant volume?

Ans. 67490 cals.

PROBLEM 141.—The heat of solution of $MgSO_4$ is 20280 cals., of $MgSO_4, H_2O$, 13300 cals., and of $MgSO_4, 7H_2O$, − 3800 cals. What is the heat of hydration

(*a*) of $MgSO_4$ to $MgSO_4, H_2O$,
(*b*) of $MgSO_4$ to $MgSO_4, 7H_2O$,
(*c*) of $MgSO_4, H_2O$ to $MgSO_4, 7H_2O$?

Ans. (*a*) 6980 cals., (*b*) 24080 cals., (*c*) 17100 cals.

PROBLEM 142.—From the following data calculate the heat of formation of potassium hydroxide:—

$$K + H_2O + Aq = KOH\ Aq + H + 48100 \text{ cals.}$$
$$H_2 + O = H_2O + 68400 \text{ cals.}$$
$$KOH + Aq = KOH\ Aq + 13300 \text{ cals.}$$

Ans. 103200 cals.

PROBLEM 143.—The heat of solution of $BaCl_2$ is 2070 cals., and its heat of hydration to $BaCl_2, 2H_2O$ is 6970 cals. What is the heat of solution of the latter salt?

Ans. − 4900 cals.

PROBLEM 144.—At ordinary temperature the heats of combustion of 12 grams of diamond, graphite and amorphous carbon are 94310, 94810 and 97650 cals. respectively. What is the heat of formation (*a*) of diamond from amorphous carbon, (*b*) of graphite from amorphous carbon, (*c*) of diamond from graphite at ordinary temperature?

Ans. (*a*) 3340, (*b*) 2840, (*c*) 500 cals.

PROBLEM 145.—From the following data calculate the heat of formation of anhydrous Al_2Cl_6:—

$$2Al + 6HCl\ Aq = Al_2Cl_6Aq + 3H_2 + 239760 \text{ cals.}$$
$$H_2 + Cl_2 = 2HCl + 44000 \text{ cals.}$$
$$HCl + Aq = HCl\ Aq + 17315 \text{ cals.}$$
$$Al_2Cl_6 + Aq = Al_2Cl_6Aq + 153690 \text{ cals.}$$

Ans. 321960 cals.

PROBLEM 146.—The heats of solution of

$$Na_2SO_4;\ Na_2SO_4, H_2O;\ \text{and}\ Na_2SO_4, 10H_2O$$

are 460, − 1900 and − 18760 cals. respectively. What are the heats of hydration of Na_2SO_4 (*a*) to monohydrate, (*b*) to decahydrate?

Ans. (*a*) 2360, (*b*) 19220 cals.

PROBLEM 147.—The heat of formation of H_2O is 68360 cals. and of CO_2, 96960 cals., both at 17° C. and constant pressure. The heat of combustion of methane at 17° C. and constant pressure is 211930 cals. Calculate the heat of formation of methane at 17° (*a*) at constant pressure, (*b*) at constant volume.

Ans. (*a*) 21750 cals., (*b*) 21170 cals.

PROBLEM 148.—The heat of neutralisation of HCl with NaOH is 13680 cals., that of acetic acid with the same base is 13400 cals., and of butyric acid 13800 cals. What are the

heats of dissociation (*a*) of acetic, (*b*) of butyric acid, if both are regarded as practically undissociated?

Ans. (*a*) − 280, (*b*) 120 cals.

PROBLEM 149.—The heats of neutralisation of NaOH and NH_4OH by HCl are 13680 and 12270 cals. respectively. What is the heat of dissociation of NH_4OH, if it is assumed to be practically undissociated?

Ans. − 1410 cals.

PROBLEM 150.—The heat of neutralisation of HNO_3 by NaOH is 13680 cals. and of $CHCl_2.COOH$, 14830 cals. When one equivalent of NaOH is added to a dilute solution containing one equivalent of HNO_3 and one equivalent of $CHCl_2.COOH$, 13960 cals. are liberated. In what ratio is the base distributed between the two acids?

Ans. $HNO_3 : CHCl_2.COOH = 0{\cdot}756 : 0{\cdot}244 = 3{\cdot}1 : 1$.

PROBLEM 151.—The heats of formation of CO_2, liquid H_2O and C_2H_4 at 17° and constant pressure are 96960, 68360 and − 2710 cals. respectively. What is the heat of combustion of C_2H_4 at 17° to CO_2 and liquid H_2O (*a*) at constant pressure, (*b*) at constant volume?

Ans. (*a*) 333350 cals., (*b*) 332190 cals.

PROBLEM 152.—From the following data calculate the heat of formation of HNO_2 Aq.

$$NH_4NO_2 = N_2 + 2H_2O + 71770 \text{ cals.}$$
$$2H_2 + O_2 = 2H_2O + 136720 \text{ cals.}$$
$$N_2 + 3H_2 + Aq = 2NH_3Aq + 40640 \text{ cals.}$$
$$NH_3Aq + HNO_2Aq = NH_4NO_2Aq + 9110 \text{ cals.}$$
$$NH_4NO_2 + Aq = NH_4NO_2Aq - 4750 \text{ cals.}$$

Ans. $H + N + O_2 + Aq = HNO_2Aq + 30770$ cals.

PROBLEM 153.—The heat of neutralisation of hydrochloric acid by sodium hydroxide is 13780 cals., and of monochloracetic acid 14280 cals. When one equivalent of hydrochloric acid is added to one equivalent of sodium monochloracetate in dilute aqueous solution there is a heat absorption of 455 cals. How much of the acetate is decomposed according to the equation

$$CH_2Cl.COONa + HCl = NaCl + CH_2Cl.COOH?$$

Ans. 0·91 equivalent.

PROBLEM 154.—From the following data :—

$$C + O_2 = CO_2 + 96960 \text{ cals.},$$
$$2H_2 + O_2 = 2H_2O + 136720 \text{ cals.},$$
$$2C_6H_6 + 15O_2 = 12CO_2 + 6H_2O + 1598700 \text{ cals.},$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O + 620100 \text{ cals.},$$

all at 17° and constant pressure, calculate the heat evolved at 17° in the reaction

$$3C_2H_2 = C_6H_6,$$

(*a*) at constant pressure, (*b*) at constant volume.

Ans. (*a*) 130800 cals., (*b*) 129640 cals.

PROBLEM 155.—From the following data calculate the heat of formation of As_2O_3 :—

$$As_2O_3 + 3H_2O + Aq = 2H_3AsO_3Aq - 7550 \text{ cals.}$$
$$As + 3Cl = AsCl_3 + 71390 \text{ cals.}$$
$$AsCl_3 + 3H_2O + Aq = H_3AsO_3Aq + 3HCl\,Aq + 17580 \text{ cals.}$$
$$H + Cl = HCl + 22000 \text{ cals.}$$
$$HCl + Aq = HCl\,Aq + 17315 \text{ cals.}$$
$$H_2 + O = H_2O + 68360 \text{ cals.}$$

Ans. 154680 cals.

CHAPTER VII

VELOCITY OF REACTION

Monomolecular Reaction

THE equation for the velocity at any instant of a monomolecular reaction which goes to practical completion is, at constant temperature,

$$(1)\quad \frac{dx}{dt} = k(a - x).$$

a is the initial concentration of the substance undergoing change and x the amount changed after the time-interval t from the commencement of the reaction. dx represents the infinitely small quantity of substance transformed in the infinitely small time-interval dt, starting from t. x is not, of course, the absolute amount changed but is the decrease in the initial concentration due to the change. k is called the velocity-constant of the reaction.

This equation gives, on integration,

$$(1)\quad -\log_e(a - x) = kt + \text{constant.}$$

But when $t = 0$, $x = 0$,

$$(2)\quad \therefore\ -\log_e a = \text{constant.}$$

By subtracting (2) from (1) we obtain

$$\log_e \frac{a}{a - x} = kt \text{ or } k = \frac{1}{t}\log_e \frac{a}{a - x},$$

or, converting to common logarithms,

$$(2)\quad \frac{2{\cdot}302}{t}\log \frac{a}{a - x} = k.$$

If x_1 and x_2 are the amounts transformed after the time-intervals t_1 and t_2 respectively, then from (2),

$$2{\cdot}302 \log \frac{a}{a - x_1} = kt_1 \text{ and } 2{\cdot}302 \log \frac{a}{a - x_2} = kt_2,$$

and, by subtracting the former equation from the latter,

$$2{\cdot}302 \log \frac{a - x_1}{a - x_2} = k(t_2 - t_1),$$

$$\text{or, } (3) \quad \frac{2{\cdot}302}{t_2 - t_1} \log \frac{a - x_1}{a - x_2} = k.$$

In the case of a monomolecular reaction the numerical value of k is independent of the unit chosen to express the concentrations a and x. Thus if a unit n times less than that used in equation (2) is chosen, we obtain

$$\frac{2{\cdot}302}{t} \log \frac{na}{n(a - x)} = \frac{2{\cdot}302}{t} \log \frac{a}{a - x} = k.$$

Bimolecular Reaction

At constant temperature the velocity at any instant of a bimolecular reaction which goes to practical completion is given by the equation

$$(4) \quad \frac{dx}{dt} = k(a - x)(b - x).$$

a and b are the initial concentrations of the reacting substances, x the diminution in concentration of the reacting substances after the time-interval t from the commencement of the reaction, due to their transformation into the products of the reaction, and k the velocity-constant.

Equation (4) gives, on integration,

$$k = \frac{1}{(a - b)t} \log_e \frac{(a - x)b}{(b - x)a},$$

$$(5) \quad = \frac{2{\cdot}302}{(a - b)t} \log \frac{(a - x)b}{(b - x)a}.$$

When the initial concentrations of the reacting substances are the same, i.e. when $a = b$, equation (4) becomes

$$\frac{dx}{dt} = k(a - x)^2,$$

which gives, on integration,

$$(6) \quad k = \frac{1}{t} \cdot \frac{x}{a(a - x)}.$$

For a bimolecular reaction the numerical value of k depends on the unit of concentration chosen for a, b and x. Thus if

a unit $1/n^{th}$ of that used in equations (5) and (6) is employed, these equations become

$$(7)\quad k' = \frac{2{\cdot}302}{n(a-b)t}\log\frac{n(a-x)bn}{n(b-x)an} = \frac{2{\cdot}302}{n(a-b)t}\log\frac{(a-x)b}{(b-x)a},$$

$$\text{and (8)}\quad k' = \frac{1}{t}\cdot\frac{nx}{na(a-x)n} = \frac{1}{t}\cdot\frac{x}{na(a-x)}.$$

By dividing (7) by (5) or (8) by (6) we obtain

$$k' = \frac{k}{n}.$$

Therefore, when using a particular value of k for a given reaction, the concentrations should be expressed in the same unit as was employed in obtaining that value of k.

Velocity of Reaction—Examples

PROBLEM 156.—When a solution of dibromsuccinic acid is heated the acid decomposes into brom-maleic acid and hydrobromic acid according to the equation

$$\begin{matrix}\text{CHBr}\,.\,\text{COOH}\\ |\\ \text{CHBr}\,.\,\text{COOH}\end{matrix} = \begin{matrix}\text{CH}\,.\,\text{COOH}\\ \|\\ \text{CBr}\,.\,\text{COOH}.\end{matrix} + \text{HBr}.$$

At 50° the initial titre of a definite volume of the solution was $T_o = 10{\cdot}095$ c.c. of standard alkali. After t minutes the titre of the same volume of solution was T_t c.c. of standard alkali.

t	0	214	380
T_t	10·095 (T_o)	10·37	10·57

(*a*) Calculate the velocity-constant of the reaction. (*b*) After what time is $\frac{1}{3}$ of the dibromsuccinic acid decomposed?

SOLUTION 156.—(*a*) The initial equivalent concentration a of the dibromsuccinic acid is proportional to T_o. Since 1 molecule of dibasic dibromsuccinic acid gives 1 molecule of dibasic brom-maleic acid and 1 molecule of monobasic hydrobromic acid, the increase in the titre $(T_t - T_o)$ after time t is proportional to the equivalent concentration of the hydrobromic acid at time t. But the formation of 1 equivalent of hydrobromic acid means the disappearance of 2 equivalents of dibromsuccinic acid, therefore x, the decrease in the equivalent concentration of the dibromsuccinic acid after time t, is proportional to 2 $(T_t - T_o)$. Therefore, from (2),

$$k = \frac{2{\cdot}302}{t} \log \frac{a}{a - x} = \frac{2{\cdot}302}{t} \log \frac{T_o}{T_o - 2(T_t - T_o)}$$
$$= \frac{2{\cdot}302}{t} \log \frac{T_o}{3T_o - 2T_t}.$$

For $t = 214$ minutes

$$k = \frac{2{\cdot}302}{214} \log \frac{10{\cdot}095}{3 \times 10{\cdot}095 - 2 \times 10{\cdot}37} = \mathbf{0{\cdot}000261},$$

and for $t = 380$ minutes

$$k = \frac{2{\cdot}302}{380} \log \frac{10{\cdot}095}{3 \times 10{\cdot}095 - 2 \times 10{\cdot}57} = \mathbf{0{\cdot}000260}.$$

The mean velocity-constant is, therefore, $k = \mathbf{0{\cdot}000260}$.

(*b*) When $\frac{1}{3}$ of the acid is decomposed the concentration of the remaining acid is $\frac{2}{3}$ of the initial concentration a; therefore $(a - x) = \frac{2}{3}a$ and

$$k = \frac{2{\cdot}302}{t} \log \frac{a}{\frac{2}{3}a} = \frac{2{\cdot}302}{t} \log \frac{3}{2},$$

$$\text{or, } \mathbf{t} = \frac{2{\cdot}302}{k} \log \frac{3}{2} = \frac{2{\cdot}302}{0{\cdot}000260} \log \frac{3}{2} = \mathbf{1559} \text{ minutes.}$$

See also problem 234, p. 108.

PROBLEM 157.—A $b = 0{\cdot}01$ N-solution of ethyl acetate is saponified to the extent of $c = 10$ per cent. in $t_1 = 23$ minutes by an $a = 0{\cdot}002$ N-solution of sodium hydroxide. In how many, (t_2), minutes would it be saponified to the same extent by an $a' = 0{\cdot}005$ N-solution of potassium hydroxide?

SOLUTION 157.—The saponification of ethyl acetate takes place according to the equation

$$CH_3 . COOC_2H_5 + H_2O = CH_3 . COOH + C_2H_5OH.$$

In alkaline solutions free acetic acid is not formed, but the alkali salt, which is almost completely dissociated into its ions. The equation for the reaction may, therefore, be written in the ionic form

$$CH_3 . COOC_2H_5 + OH' = CH_3 . COO' + C_2H_5OH.$$

If x is the quantity of ethyl acetate saponified at the time t, the velocity of saponification $\frac{dx}{dt}$ is given by the equation

$$\frac{dx}{dt} = k[OH'][CH_3 . COOC_2H_5],$$
$$= k(a - x)(b - x),$$

if the NaOH is regarded as completely dissociated. The square brackets denote the concentration of the enclosed substance. The integration of this differential equation is carried out as follows :—

$$\frac{dx}{(a-x)(b-x)} = k\,.\,dt$$

$$\frac{dx}{(a-b)}\left(\frac{1}{b-x} - \frac{1}{a-x}\right) = k\,.\,dt$$

and, on integration,

$$(1)\quad -\frac{1}{a-b}\left[\log_e(b-x) - \log_e(a-x)\right] = kt + \text{constant.}$$

At the time $t = 0$, $x = 0$, and, therefore,

$$(2)\quad -\frac{1}{a-b}\left[\log_e b - \log_e a\right] = \text{constant.}$$

By subtracting (2) from (1) we obtain

$$\frac{1}{a-b}\log_e\frac{b(a-x)}{a(b-x)} = kt,$$

and, converting to common logarithms,

$$(3)\quad k = \frac{2{\cdot}302}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}.$$

From the data given in the problem, at the time $t_1 = 23$ minutes $x = \frac{c}{100}b = \frac{10}{100}b = 0{\cdot}1\,b$. The velocity-constant k may, therefore, be calculated from equation (3), since all the other quantities are known.

For this particular case we have

$$\begin{aligned} k &= \frac{2{\cdot}302}{t_1(a-b)}\log\frac{b(a-0{\cdot}1\,b)}{a(b-0{\cdot}1\,b)} \\ &= \frac{2{\cdot}302}{23\times -0{\cdot}008}\log\frac{0{\cdot}01\times 0{\cdot}001}{0{\cdot}002\times 0{\cdot}009} \\ &= -12{\cdot}51\log 0{\cdot}556 \\ &= -12{\cdot}51\times -0{\cdot}255 = \mathbf{3{\cdot}19.} \end{aligned}$$

It is now possible to calculate the time t_2 in which the same ester solution would be saponified to the same extent by $a' = 0{\cdot}005$ N-KOH solution. Since KOH, like NaOH, may be regarded as completely dissociated in dilute solution, we obtain again

$$\frac{dx}{dt} = k(a'-x)(b-x),$$

or, integrated,

$$t_2 = \frac{1}{k(a' - b)} \log_e \frac{b(a' - x)}{a'(b - x)},$$

$$= \frac{2{\cdot}302}{3{\cdot}19 \times -0{\cdot}005} \log \frac{0{\cdot}01 \times 0{\cdot}004}{0{\cdot}005 \times 0{\cdot}009},$$

$$= -144 \log 0{\cdot}89 = 144 \times 0{\cdot}051 = 7{\cdot}34 \text{ minutes.}$$

PROBLEM 158 (cf. preceding problem).—What do the times t_1 and t_2 in the preceding problem become (1) if all the concentrations a, b and a' are diminished to $\frac{1}{n} = \frac{1}{10}$ of their values there, (2) if the temperature is raised by 15° C., if it is assumed that the velocity-constant for any temperature is doubled by a rise of 10° C.?

SOLUTION 158.—(1) If all the concentrations in the preceding problem are diminished to $\frac{1}{n} = \frac{1}{10}$ of their values there, the new values are

$$a = 0{\cdot}0002,\ b = 0{\cdot}001,\ a' = 0{\cdot}0005,\ x = 0{\cdot}0001.$$

As in the preceding problem we obtain

$$t_1 = \frac{2{\cdot}302}{k(a - b)} \log \frac{b(a - x)}{a(b - x)},$$

$$= \frac{2{\cdot}302}{3{\cdot}19 \times -0{\cdot}0008} \log \frac{0{\cdot}001 \times 0{\cdot}0001}{0{\cdot}0002 \times 0{\cdot}0009},$$

$$= -900 \log 0{\cdot}556 = \mathbf{230} \text{ minutes.}$$

and similarly,

$$t_2 = -1440 \log 0{\cdot}89 = \mathbf{73{\cdot}4} \text{ minutes.}$$

If, therefore, all the concentrations are diminished to $\frac{1}{n}$ of their previous values, the time required for the reaction to proceed to the same extent is increased to n times its previous value.

(2) If a rise of temperature of 10° C. doubles the velocity-constant k, i.e. if

$$k_{t^\circ + 10} = 2k_{t^\circ},$$

the relation between k and t° may be deduced as follows:—

$$\log k_{t^\circ + 10} = \log 2 + \log k_{t^\circ},$$

$$\log k_{t^\circ + 10} - \log k_{t^\circ} = \log 2$$

$$\text{i.e. } \frac{d \log k}{dt^\circ} = \frac{\log 2}{10} = 0{\cdot}0301,$$

and, on integration,

$$(1)\ \log k = 0{\cdot}0301t^\circ + \text{constant}.$$

For t°_1, the temperature corresponding to the values in the preceding problem, $k_1 = 3{\cdot}19$, and, therefore,

$$(2)\ \log k_1 = 0{\cdot}0301t^\circ_1 + \text{constant}.$$

By subtracting (2) from (1)

$$\log \frac{k}{k_1} = 0{\cdot}0301(t^\circ - t^\circ_1).$$

For $t^\circ - t^\circ_1 = 15^\circ$ C. we therefore obtain

$$\log k = \log k_1 + 15 \times 0{\cdot}0301 = 0{\cdot}504 + 0{\cdot}452 = 0{\cdot}956,$$
$$\therefore k = 9{\cdot}04.$$

If t and t_1 are the times required for the reaction to proceed to the same extent at the temperatures t° and t°_1, and k and k_1 are the velocity-constants at these temperatures, then if a, b and, therefore, since the reaction proceeds to the same extent, x are the same in the two cases, it is evident from the equations

$$t = \frac{1}{k(a-b)} \log_e \frac{b(a-x)}{a(b-x)}$$

and

$$t_1 = \frac{1}{k_1(a-b)} \log_e \frac{b(a-x)}{a(b-x)}$$

that

$$\frac{t}{t_1} = \frac{k_1}{k}.$$

The times required for the reaction to proceed to the same extent at the two temperatures, are, therefore, *ceteris paribus*, inversely proportional to the velocity-constants.

For 0·002 N-NaOH, where $t_1 = 23$, $k_1 = 3{\cdot}19$ and $k = 9{\cdot}06$, we obtain

$$t = \frac{3{\cdot}19}{9{\cdot}06} \times 23 = 8{\cdot}1 \text{ minutes},$$

and for 0·005 N-KOH, where $t_1 = 7{\cdot}34$, $k_1 = 3{\cdot}19$ and $k = 9{\cdot}06$,

$$t = \frac{3{\cdot}19}{9{\cdot}06} \times 7{\cdot}34 = 2{\cdot}6 \text{ minutes}.$$

Problems for Solution

PROBLEM 159.—From the following data show that the decomposition of H_2O_2 in aqueous solution is a monomolecular reaction :—

Time in minutes,	0	10	20
n	22·8	13·8	8·25 c.c.

n is the number of c.c. of $KMnO_4$ required to decompose a definite volume of the H_2O_2 solution.

PROBLEM 160. — The decomposition of AsH_3 into solid arsenic and hydrogen may be followed by measuring the pressure at constant volume from time to time. In an experiment at 310° the pressures p in mm. of Hg were obtained after the times t hours. Show from these figures that the reaction is of the first order.

t	0	5·5	6·5	8 hours.
p	733·32	805·78	818·11	835·34 mm.

PROBLEM 161.—The conversion of acetchloranilide into p-chloracetanilide according to the equation

$$C_6H_5 . NCl(COCH_3) = C_6H_4Cl . NH(COCH_3)$$

may be followed by removing a measured quantity of the solution from time to time, adding it to a solution of KI, and titrating the liberated iodine with standard thiosulphate. The volume of thiosulphate used is proportional to the concentration of the acetchloranilide. Thus after t hours from the commencement of the reaction y c.c. of thiosulphate were required.

t	1	4
y	35·6	13·8

In what time is the conversion half completed ?

Ans. 2·195 hours.

PROBLEM 162.—The decomposition of diacetonealcohol into acetone according to the equation

$$CH_3 . CO . CH_3 . C(CH_3)_2 . OH = 2CH_3 . CO . CH_3$$

is accompanied by a considerable increase in volume. The reaction is catalytically accelerated by OH′-ions, the velocity-constant being proportional to the concentration of OH′-ions. By allowing the reaction to take place in a dilatometer the expansion may be observed. The quantity of diacetone-

alcohol present at any time is proportional to the expansion from that time to the end of the reaction. The following table gives the dilatometer readings R at the times t, obtained with a mixture of 20 c.c. 0·1 N-NaOH and 1·0526 grams of diacetonealcohol. Calculate the velocity-constant for 0·1 N-NaOH.

t	0	10	20	30	40	50	60	∞ mins.
R	0	60·8	97·7	119·9	133·4	141·4	146·1	153·8

Ans. Mean $k = 0{\cdot}05030$.

PROBLEM 163. — Potassium persulphate and potassium iodide interact with liberation of iodine. 25 c.c. of a solution, which was N/30 with respect to both persulphate and iodide, were titrated from time to time with N/100 $Na_2S_2O_3$. From the following results show that the reaction is bimolecular. t is the time of titration and x the number of c.c. of thiosulphate used.

t	9	16	32	50
x	4·52	7·80	14·19	20·05.

PROBLEM 164.—In the saponification of ethyl acetate by NaOH at 10°, y c.c. of 0·043 N-HCl were required to neutralise 100 c.c. of the reaction mixture t minutes after the commencement of the reaction.

t	0	4·89	10·37	28·18	∞
y	61·95	50·59	42·40	29·35	14·92.

Calculate the velocity-constant when the concentrations are expressed in gram-molecules per litre.

Ans. Mean $k = 2{\cdot}38$.

PROBLEM 165 (cf. preceding problem).—1 litre of N/20 ethyl acetate is mixed at 10° with (*a*) 1 litre of N/20 NaOH, (*b*) 1 litre N/10 NaOH, (*c*) 1 litre N/25 NaOH. In what time is half the ester saponified in each case?

Ans. (*a*) 16·8 mins., (*b*) 6·81 mins., (*c*) 24·2 mins.

See also problems 319, 320.

CHAPTER VIII

LAW OF MASS-ACTION. — EQUILIBRIUM-CONSTANT. — INFLUENCE OF TEMPERATURE ON EQUILIBRIUM-CONSTANT.— AFFINITY, CHANGE OF FREE ENERGY OR MAXIMUM WORK OF A REACTION.—PARTITION LAW.—SOLUBILITY OF GASES.

Law of Mass-action—Equilibrium-constant

IF a number of substances, for example, the four substances A, B, C and D, react according to the equation

$$mA + nB = pC + qD,$$

then, at equilibrium, the following relation exists between the concentrations (number of units of mass in unit volume) of these four substances (Guldberg and Waage),

$$(1) \quad \frac{[C]^p\,[D]^q}{[A]^m\,[B]^n} = K_c.$$

The square brackets denote the concentrations of the enclosed substances. m, n, p and q are the number of molecules of A, B, C and D which take part in the reaction. K_c is called the constant of the law of mass-action, or the equilibrium-constant for the reaction. For a given reaction, the value of K_c depends on the temperature, being constant for a given temperature, and on the units of mass and volume used to express the concentrations.

If v is the number of units of volume occupied by the reaction mixture at equilibrium, and a, b, c and d the number of units of mass of A, B, C and D respectively present in this volume at equilibrium, the concentrations of A, B, C, and D are

$$[A] = \frac{a}{v}, \quad [B] = \frac{b}{v}, \quad [C] = \frac{c}{v}, \quad [D] = \frac{d}{v},$$

and, from (1),

$$(2)\quad \frac{[C]^p[D]^q}{[A]^m[B]^n} = \frac{\left(\frac{c}{v}\right)^p\left(\frac{d}{v}\right)^q}{\left(\frac{a}{v}\right)^m\left(\frac{b}{v}\right)^n} = \frac{c^p d^q}{a^m b^n} \times \frac{v^{m+n}}{v^{p+q}} = K_c.$$

If m + n = p + q, that is, if the total number of molecules on each side of the equation is the same, equation (2) becomes

$$(3)\quad \frac{[C]^p\,[D]^q}{[A]^m\,[B]^n} = \frac{c^p d^q}{a^m b^n} = K_c$$

that is, for a given temperature and unit of mass, the value of the constant K_c is independent of the unit of volume used in expressing the concentrations.

In all other cases, as can be readily seen from (2), the value of K_c is dependent on the unit of volume. Thus if K_c is the value of the equilibrium-constant for a given unit of volume, then for a unit of volume x times smaller, the constant is $K_c \times x^{m+n-p-q}$, for

$$[A] = \frac{a}{xv},\quad [B] = \frac{b}{xv},\quad [C] = \frac{c}{xv},\quad [D] = \frac{d}{xv},$$

and (2) becomes

$$(4)\quad \frac{c^p d^q}{a^m b^n} \times \frac{(xv)^{m+n}}{(xv)^{p+q}} = K'_c = K_c \times x^{m+n-p-q}$$

Thus if K_c is the value of the constant when the concentrations are expressed in gram-molecules per litre, the value of the constant is $K_c \times 1000^{m+n-p-q}$ when the concentrations are expressed in gram-molecules per c.c.

The unit of concentration usually employed, and the one which will be used in the following examples, is the gram-molecule per litre.

That the value of K_c depends on the unit of mass used in expressing the concentrations may be shown by expressing the concentrations in grams per litre instead of gram-molecules per litre. (2) then becomes

$$\frac{\left(\frac{cM_C}{v}\right)^p\left(\frac{dM_D}{v}\right)^q}{\left(\frac{aM_A}{v}\right)^m\left(\frac{bM_B}{v}\right)^n} = K'_c = K_c\left(\frac{M_C{}^p M_D{}^q}{M_A{}^m M_B{}^n}\right),$$

where M_A, M_B, M_C and M_D are the molecular weights of A, B, C and D respectively.

In any particular case the unit of concentration employed must be that used in obtaining the value of K_c involved.

From (3) it is evident that for given amounts of the reacting substances the position of equilibrium, or the quantities of the reacting substances present at equilibrium, is independent of the volume of the reaction-mixture when the same number of molecules occurs on each side of the reaction-equation. In all other cases we see from (2) that the position of equilibrium is dependent on the volume of the reaction-mixture.

In the case of gases, their partial pressures at equilibrium may be substituted for their concentrations in equations (1), (2) and (3). The numerical value of the equilibrium-constant will, of course, depend on whether we use partial pressures or concentrations. The relation between the different values may be found as follows. If we assume that A, B, C, and D are all gases, and that T is the absolute temperature of the equilibrium-mixture, then for concentrations in gram-molecules per litre equation (2) holds. If the partial pressures in atmospheres of the four substances are p_A, p_B, p_C, p_D, then

$$\frac{(p_C)^p(p_D)^q}{(p_A)^m(p_B)^n} = K_p.$$

But according to (2), page 1, if a, b, c and d are the numbers of gram-molecules of A, B, C and D present in v litres at equilibrium,

$$p_A = \frac{aRT}{v},\ p_B = \frac{bRT}{v},\ p_C = \frac{cRT}{v},\ p_D = \frac{dRT}{v},$$

$$\therefore K_p = \frac{\left(\frac{cRT}{v}\right)^p\left(\frac{dRT}{v}\right)^q}{\left(\frac{aRT}{v}\right)^m\left(\frac{bRT}{v}\right)^n} = \frac{\left(\frac{c}{v}\right)^p\left(\frac{d}{v}\right)^q(RT)^{p+q}}{\left(\frac{a}{v}\right)^m\left(\frac{b}{v}\right)^n(RT)^{m+n}}$$

$$= K_c(RT)^{p+q-m-n}$$

Only when $p + q = m + n$ is $K_p = K_c$.

If the equilibrium-constant used in a particular case is that obtained by using concentrations of the reacting substances in gram-molecules per litre, then the active masses of the reacting substances must always be expressed in gram-molecules per litre when using this value of the equilibrium-constant.

Similarly, if the equilibrium-constant used was obtained by employing partial pressures instead of concentrations, the active masses of the reacting substances must always be expressed in partial pressures when using this value of the equilibrium-constant.

If one or more of the reacting substances are present in the solid state, their active masses, and, therefore, their concentrations at equilibrium, are constant, and may be omitted from the equation. If, for example, A and C in the reaction

$$mA + nB = pC + qD$$

are solid substances, the law of mass-action requires

$$(5)\quad \frac{[D]^q}{[B]^n} = K_c.$$

Equilibrium-constant and Temperature

The equilibrium-constant K_c or K_p is dependent on the temperature according to the equations (van't Hoff)

$$(6)\quad \frac{d \log_e K_c}{dT} = \frac{-Q_v}{RT^2} \text{ and } \frac{d \log_e K_p}{dT} = \frac{-Q_p}{RT^2}.$$

Q_v and Q_p are the heats evolved in the reaction from left to right at constant volume and constant pressure respectively; in the reaction

$$mA + nB = pC + qD,$$

for example, in the transformation of m gram-molecules of A and n gram-molecules of B into p gram-molecules of C and q gram-molecules of D. Q_v and Q_p are assumed to be independent of the temperature (see p. 25). R is the gas-constant (1·985 or, approximately, 2 for calories) and T the absolute temperature. On integration between the absolute temperatures T and T_1, for which the respective equilibrium-constants are K_c and K_{c1} (for concentrations) and K_p and K_{p1} (for partial pressures), we obtain on changing from natural to common logarithms

$$(7)\quad \log K_c - \log K_{c1} = \frac{Q_v}{2{\cdot}3R}\left(\frac{1}{T} - \frac{1}{T_1}\right) = \frac{Q_v}{2{\cdot}3R}\left(\frac{T_1 - T}{TT_1}\right),$$

$$(8)\quad \log K_p - \log K_{p1} = \frac{Q_p}{2{\cdot}3R}\left(\frac{1}{T} - \frac{1}{T_1}\right) = \frac{Q_p}{2{\cdot}3R}\left(\frac{T_1 - T}{TT_1}\right).$$

What was said about L in equation (5), p. 25, applies equally to Q_v and Q_p in the above equations.

The following are some of the applications of these equations. In all cases the heat-effect is for the mean temperature $\frac{T+T_1}{2}$. The application to ordinary chemical equilibria is obvious from the explanations given above. The equations apply also, however, to many physical equilibria. As we have already seen (p. 25), in the case of vaporisation

$$(9)\quad \log p - \log p_1 = \frac{L}{2{\cdot}3R}\left(\frac{T_1 - T}{TT_1}\right),$$

where p and p_1 are the vapour-pressures of the liquid at T and T_1 respectively, and L is the latent heat of evaporation per gram-molecule (at constant pressure). For the sublimation of a solid the same equation holds, L being the molecular heat of sublimation.

For the solubility of solids we have

$$(10)\quad \log c - \log c_1 = \frac{Q}{2{\cdot}3R}\left(\frac{T_1 - T}{TT_1}\right),$$

where c and c_1 are the concentrations of the saturated solutions at T and T_1 respectively, and Q is the heat of solution per gram-molecule.

In the case of a difficultly soluble strong binary electrolyte, where the dissociation in the saturated solution may be regarded as practically complete, we have (p. 121)

$$K = c^2 \text{ and } K_1 = c_1{}^2 \text{ (solubility-products)},$$

where c and c_1 are the solubilities at T and T_1 respectively. Hence

$$(11)\quad \log c^2 - \log c_1{}^2 = \frac{Q}{2{\cdot}3R}\left(\frac{T_1 - T}{TT_1}\right),$$

where Q is the heat of ionisation per gram-molecule. The heat of precipitation of the solid from its ions has the same value as Q, but the opposite sign.

For electrolytes which obey the dilution-law we have

$$(12)\quad \log K - \log K_1 = \frac{Q}{2{\cdot}3R}\left(\frac{T_1 - T}{TT_1}\right),$$

where K and K_1 are the dissociation-constants at T and T_1 respectively, and Q the heat of ionisation per gram-molecule.

Affinity, or Change of Free Energy

At a definite temperature T, the affinity, or change of free energy, of a chemical reaction, for example, of the reaction

$$mA + nB = pC + qD$$

is

$$(13)\quad A = RT\log_e K_c + RT\log_e \frac{[A]^m\,[B]^n}{[C]^p\,[D]^q}$$

or

$$(14)\quad A = RT\log_e K_p + RT\log_e \frac{(A)^m\,(B)^n}{(C)^p\,(D)^q}.$$

K_c is the equilibrium-constant for concentrations in gram-molecules per litre, and K_p that for partial pressures in atmospheres. A is the maximum work which can be performed by the reversible transformation of m gram-molecules of A and n gram-molecules of B at the concentrations [A] and [B] gram-molecules per litre, or at the partial pressures (A) and (B) atmospheres respectively into p gram-molecules of C and q gram-molecules of D at the concentrations [C] and [D] gram-molecules per litre, or at the partial pressures (C) and (D) atmospheres.

Partition Law

When a soluble substance is distributed between two non-miscible solvents, in each of which it has the same molecular weight, the ratio of the concentrations c_1 and c_2 of the solute in the two solvents has a constant value for a given temperature, or

$$(15)\quad \frac{c_1}{c_2} = K.$$

This is Nernst's partition law. K is called the partition-coefficient of the dissolved substance for the two solvents.

If the solute has not the same molecular weight in the two solvents, but has, say, its normal molecular weight in the first solvent, whilst in the second solvent it is more or less associated to complex molecules according to the equation

$$nS \rightleftarrows S_n,$$

then the ratio $\frac{c_1}{c_2}$ is no longer constant. For each definite kind of molecule S, S_2, S_3 . . . S_n however, there is a constant

partition-coefficient for the two solvents, and the ratio of the concentrations found experimentally is influenced by all these. If one particular type of complex, say S_n, predominates largely in the second solvent, the concentration of the solute in this solvent will be practically that of the S_n molecules. According to the law of mass-action, there exists between the simple and the complex molecules in the second solvent the relation

$$[S]_2^n = k[S_n]$$

and, according to the partition law, between the simple molecules in the first solvent and those in the second solvent the relation

$$\frac{[S]_1}{[S]_2} = K,$$

where $[S]_1$ and $[S]_2$ are the concentrations of the simple molecules in the first and second solvent respectively, and K is the partition-coefficient for this type of molecule. From these two equations we obtain

$$\frac{[S]_1}{\sqrt[n]{[S_n]}} = \sqrt[n]{k} \times K = K_1.$$

Since the S_n molecules are supposed to largely predominate in the second solvent, the total concentration in this solvent will be practically that of the S_n molecules. If, then, c_1 and c_2 are the total concentrations of the solute in the first and second solvents respectively we obtain

$$(16)\quad \frac{c_1}{\sqrt[n]{c_2}} = \text{constant}.$$

c_1 and c_2 may be expressed in any unit, for example, grams or gram-molecules (of normal molecular weight) per litre.

Solubility of Gases

The mass of a gas dissolved by a given volume of a liquid at a definite temperature is proportional to the pressure of the gas. This is Henry's law. Since the concentrations of the gas in the liquid and in the space above the liquid are both proportional to the pressure of the gas, Henry's law may be stated in the following form, which corresponds to Nernst's partition law. For a given temperature

$$(17)\quad \frac{\text{the concentration of the gas in the liquid}}{\text{the concentration of the gas in the space above the liquid}} = \text{constant} = s.$$

s is called the solubility-coefficient of the gas in the liquid for the given temperature.

The solubility-coefficient s of a gas in a liquid at a definite temperature $t°$ C. may be defined as the volume of gas, measured at $t°$ C. and under a pressure of p atmospheres, which is dissolved by unit volume of the liquid when the pressure of the gas on the liquid at equilibrium is p atmospheres.

That the solubility-coefficient s so defined is the same as the ratio of the concentrations of the gas in the liquid and in the space above may be shown as follows :—

At 0° C. and under 1 atmosphere pressure, 1 gram-molecule of a gas occupies 22·4 litres.

1 litre of the liquid dissolves s litres of gas measured at $t°$ C. and p atmospheres,

$$= s \times \frac{273}{273 + t} \times p \text{ litres measured at 0° C. and 1 atmos.}$$

$$= s \times \frac{273}{273 + t} \times \frac{p}{22{\cdot}4} \text{ gram-molecules of gas.}$$

$\therefore$ the concentration of the gas in the liquid is

$$s \times \frac{273}{273 + t} \times \frac{p}{22{\cdot}4} \text{ gram-molecules per litre.}$$

1 gram-molecule of gas occupies 22·4 litres at 0° C. and 1 atmos.
1 gram-molecule of gas occupies

$$22{\cdot}4 \times \frac{273 + t}{273} \times \frac{1}{p} \quad \text{,,} \quad t° \text{ C. ,, } p \quad \text{,,}$$

$\therefore$ the concentration of the gas in the space above the liquid is

$$\frac{273p}{22{\cdot}4(273 + t)} \text{ gram-molecules per litre,}$$

and

$$\frac{\text{concentration of gas in the liquid}}{\text{concentration of gas in space above liquid}} = \frac{s \times 273 \times p}{(273 + t)22{\cdot}4} \times \frac{22{\cdot}4(273 + t)}{273 \times p} = s.$$

The absorption-coefficient of a gas in a liquid at $t°$ C., in terms of which the solubility of gases is often expressed, is the volume of gas, measured at 0° C. and 1 atmosphere pressure, absorbed by unit volume of the liquid when the pressure of the gas above the liquid is 1 atmosphere.

From a mixture of gases the quantity of each dissolved is proportional to its partial pressure at equilibrium.

Law of Mass-action—Equilibrium and Temperature—Affinity—Examples

PROBLEM 166.—$a = 9{\cdot}2$ grams of nitrogen peroxide occupy at $t_1 = 27°$ C. and under a pressure of $P = 1$ atmosphere a volume $v_1 = 2{\cdot}95$ litres, and at $t_2 = 111°$ C. and under the same pressure a volume $v_2 = 6{\cdot}07$ litres. Calculate the degrees of dissociation α_1 and α_2, and the dissociation-constants K_1 and K_2 of nitrogen peroxide at $t°_1$ C. and $t°_2$ C., and also its molecular heat of dissociation.

SOLUTION 166.—According to the gas laws the number n of molecules in the volume v_1, at the temperature t_1, and under the pressure P, is

$$n = \frac{Pv_1}{R(273 + t_1)}.$$

If $M = 92$ is the molecular weight of N_2O_4 and α_1 the fraction of the N_2O_4 molecules which are dissociated according to the equation $N_2O_4 = 2NO_2$, then a grams of nitrogen peroxide contain $\frac{a}{M}(1 - \alpha_1)$ molecules of N_2O_4 and $\frac{2a\alpha_1}{M}$ molecules of NO_2. From this it follows that

$$n = \frac{a}{M}(1 + \alpha_1) = \frac{Pv_1}{R(273 + t_1)}$$

and

$$\alpha_1 = \frac{MPv_1}{aR(273 + t_1)} - 1.$$

Similarly, for the temperature $t°_2$ C., we get

$$\alpha_2 = \frac{MPv_2}{aR(273 + t_2)} - 1.$$

Substituting the numerical values given in the problem, we find

$$a_1 = \frac{92 \times 1 \times 2{\cdot}95}{9{\cdot}2 \times 0{\cdot}082 \times 300} - 1 = 0{\cdot}20,$$

$$a_2 = \frac{92 \times 1 \times 6{\cdot}07}{9{\cdot}2 \times 0{\cdot}082 \times 384} - 1 = 0{\cdot}93.$$

The dissociation-constant K of the reaction

$$N_2O_4 \rightleftarrows 2NO_2$$

is

$$K = \frac{[NO_2]^2}{[N_2O_4]},$$

if the square brackets denote the concentration in moles per litre of the enclosed molecules.

For $t_1°$ C. $[N_2O_4] = \frac{a}{M}\frac{(1 - a_1)}{v_1}$ and $[NO_2] = \frac{2aa_1}{Mv_1}$, therefore

$$K_1 = \left(\frac{2aa_1}{Mv_1}\right)^2 \times \frac{Mv_1}{a(1 - a_1)} = \frac{4aa_1^2}{(1 - a_1)Mv_1}.$$

Similarly, for $t_2°$ C.,

$$K_2 = \frac{4aa_2^2}{(1 - a_2)Mv_2}.$$

Putting in the numerical values we find

$$K_1 = \frac{4 \times 9{\cdot}2 \times (0{\cdot}20)^2}{0{\cdot}80 \times 92 \times 2{\cdot}95} = 0{\cdot}0068,$$

$$K_2 = \frac{4 \times 9{\cdot}2 \times (0{\cdot}93)^2}{0{\cdot}07 \times 92 \times 6{\cdot}07} = 0{\cdot}816.$$

The heat of dissociation Q of a gram-molecule of N_2O_4 can be calculated from the dissociation-constant by van't Hoff's equation

$$\frac{d \log_e K}{dT} = \frac{-Q}{RT^2}.$$

Integration between the temperatures $T_1 = 273 + t_1$ and $T_2 = 273 + t_2$ gives, if we assume that Q does not change in this interval,

$$\log_e \frac{K_1}{K_2} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

$$Q = \frac{RT_1T_2}{T_2 - T_1} \log_e \frac{K_1}{K_2}.$$

Substituting the numerical values gives

$$Q = -\frac{1{\cdot}985 \times 300 \times 384}{84} \times 2{\cdot}3 \times \log \frac{0{\cdot}816}{0{\cdot}0068} = -13000 \text{ cals.}$$

NOTE.—The equation for the dissociation of N_2O_4 may also be written

$$N_2O_4 = NO_2 + NO_2$$

and the dissociation-constant

$$K = \frac{[NO_2]\,[NO_2]}{[N_2O_4]},$$

where each NO_2 molecule is considered separately.

We have then (see above) at t_1

$$[N_2O_4] = \frac{a}{M}\frac{(1-a_1)}{v_1},\quad [NO_2] = \frac{aa_1}{Mv_1}, [NO_2] = \frac{aa_1}{Mv_1},$$

and, similarly, at t_2

$$[N_2O_4] = \frac{a}{M}\frac{(1-a_2)}{v_2}, [NO_2] = \frac{aa_2}{Mv_2}, [NO_2] = \frac{aa_2}{Mv_2}.$$

Hence

$$K_1 = \frac{aa_1^2}{(1-a_1)Mv_1} = 0{\cdot}0017,$$

$$K_2 = \frac{aa_2^2}{(1-a_2)Mv_2} = 0{\cdot}204.$$

For a given temperature either of the expressions

$$K = \frac{4aa^2}{(1-a)Mv} \text{ or } K = \frac{aa^2}{(1-a)Mv}$$

may be used. The expression chosen must, however, be retained throughout any series of calculations dealing with the same reaction.

It is evident that the value we obtain for Q is not affected by the expression chosen for K, since the ratio K_1/K_2 remains constant.

PROBLEM 167.—If $a = 3{\cdot}6$ grams of phosphorus pentachloride is heated to $t = 200°$ C., it volatilises completely, and the vapour occupies a volume $v = 1$ litre under a pressure $P = 1$ atmosphere. At the same time it dissociates partially into phosphorus trichloride and chlorine. Calculate the degree of dissociation a and the dissociation-constant K of phosphorus pentachloride at this temperature. Express the concentrations in gram-molecules per litre.

SOLUTION 167.—As in problem 166 the number of molecules which occupy the volume v at the temperature $T°$ abs. and under the pressure P atmospheres is

$$n = \frac{Pv}{RT}.$$

If M is the molecular weight of PCl_5 and a the degree to which PCl_5 is dissociated according to the equation

$$PCl_5 = PCl_3 + Cl_2,$$

then the volume v contains $\frac{a}{M}(1 - a)$ moles of PCl_5, $\frac{aa}{M}$ moles of PCl_3 and $\frac{aa}{M}$ moles of Cl_2. Accordingly

$$n = \frac{a}{M}(1 + a) = \frac{Pv}{RT},$$

and

$$a = \frac{MPv}{aRT} - 1 = \frac{208 \times 1 \times 1}{3{\cdot}60 \times 0{\cdot}082 \times 473} - 1 = \mathbf{0{\cdot}49},$$

and the dissociation-constant at 200° C. is

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{a^2a}{M(1 - a)v}$$
$$= \frac{(0{\cdot}49)^2 \times 3{\cdot}60}{208 \times 0{\cdot}51 \times 1} = \mathbf{0{\cdot}00815}.$$

PROBLEM 168 (cf. preceding problem).—What pressure P is developed when $a = 3{\cdot}6$ grams of solid phosphorus pentachloride in $v = 1$ litre of chlorine at $t' = 18°$ C. and under a pressure $p = 1$ atmosphere, is heated at constant volume to $t = 200°$ C.?

SOLUTION 168.—According to the law of mass-action the dissociation of the PCl_5 is diminished in presence of the gaseous chlorine. In this case also the equation

$$(1)\ \frac{[PCl_3][Cl_2]}{[PCl_5]} = K$$

must be satisfied.

Let a' be the degree of dissociation of the PCl_5 at $t°$ C. in presence of the gaseous chlorine; then the number of molecules of PCl_5 in the volume v is

$$\frac{a}{M}(1 - a'),$$

and the concentration of the PCl_5 is

$$(2)\ [PCl_5] = \frac{a(1 - a')}{Mv}.$$

Similarly, the number of PCl_3 molecules in volume v is

$$n = \frac{aa'}{M},$$

and the concentration of PCl_3

$$(3)\ [PCl_3] = \frac{aa'}{Mv}.$$

The number of Cl_2 molecules is the sum of the two quantities n and n'. The n molecules are derived from the dissociation of the PCl_5 and are equal to the number of PCl_3 molecules $= \frac{aa'}{M}$. The n' molecules are derived from the chlorine originally present, and at $t°$ C. $= 273 + t' = T'$ abs. and under a pressure of p atmospheres the volume v litres contains

$$n' = \frac{pv}{RT'}, \text{ molecules of } Cl_2.$$

We get, therefore,

$$(4)\ [Cl_2] = \frac{n + n'}{v} = \frac{aa'}{Mv} + \frac{p}{RT'}.$$

From (1), (2), (3) and (4) we obtain

$$K = \frac{\frac{aa'}{Mv}\left(\frac{aa'}{Mv} + \frac{p}{RT'}\right)}{\frac{a(1 - a')}{Mv}} = a' \frac{\left(\frac{aa'}{Mv} + \frac{p}{RT'}\right)}{1 - a'}.$$

In this equation only a' is unknown, and can, therefore, be calculated as follows :—

$$K - Ka' = \frac{a(a')^2}{Mv} + \frac{a'p}{RT'},$$

$$(a')^2 + a'\left(\frac{p}{RT'} + K\right)\frac{Mv}{a} = \frac{MvK}{a},$$

$$a' = -\frac{Mv}{2a}\left(\frac{p}{RT'} + K\right) + \sqrt{\frac{M^2v^2}{4a^2}\left(\frac{p}{RT'} + K\right)^2 + \frac{MvK}{a}}$$

$$= -\frac{208 \times 1}{2 \times 3{\cdot}6}\left(\frac{1}{0{\cdot}082 \times 291} + 0{\cdot}00815\right)$$

$$+\sqrt{\frac{(208)^2}{4\times(3{\cdot}6)^2}\left(\frac{1}{0{\cdot}082\times 291}+0{\cdot}00815\right)^2+\frac{208\times 0{\cdot}00815}{3{\cdot}6}}$$
$$=-28{\cdot}85\,(0{\cdot}0419+0{\cdot}00815)+\sqrt{2{\cdot}08+0{\cdot}471}$$
$$=-1{\cdot}442+\sqrt{2{\cdot}551}$$
$$=0{\cdot}155.$$

The total number of molecules of $PCl_5 + PCl_3 + Cl_2$ is therefore,

$$N=\frac{a(1-a')}{M}+\frac{2aa'}{M}+\frac{pv}{RT''},$$
$$=\frac{3{\cdot}6\times 0{\cdot}845}{208}+\frac{2\times 3{\cdot}6\times 0{\cdot}155}{208}+\frac{1}{0{\cdot}082\times 291}$$
$$=0{\cdot}0146+0{\cdot}00536+0{\cdot}0419=0{\cdot}0619.$$

The total pressure P developed by heating a grams of PCl_5 in v litres of chlorine, at p atmospheres and $t°$ C., to 200° C. is, therefore,

$$\mathbf{P}=\frac{NRT}{v}=\frac{0{\cdot}0619\times 0{\cdot}082\times 473}{1}=\mathbf{2{\cdot}40}\text{ atmospheres.}$$

Problem 169.—Nitrogen and oxygen combine at high temperatures to form nitric oxide, according to the equation

$$N_2+O_2=2\,NO.$$

The equilibrium-constant at $T = 2675°$ abs. is

$$\frac{[NO]^2}{[N_2]\,[O_2]}=K=3{\cdot}5\times 10^{-3}.$$

What yield of NO (in percentage by volume) is obtained at this temperature and at normal pressure (1) from air, (2) from a mixture of 40 per cent. O_2 and 60 per cent. N_2 by volume, and (3) from a mixture of 80 per cent. O_2 and 20 per cent. N_2 by volume?

Solution 169.—Let the yield of NO in percentage by volume be x. Then, since the reaction takes place according to the equation

$$N_2+O_2=2\,NO,$$

from a mixture which originally contained a per cent. of O_2 and b per cent. of N_2 by volume, we get at equilibrium x per cent. of NO, $\left(a-\frac{x}{2}\right)$ per cent. of O_2 and $\left(b-\frac{x}{2}\right)$ per cent. of N_2 by volume.

Since the concentrations are proportional to these percentages by volume, we get from the law of mass-action

$$\frac{x^2}{\left(a - \frac{x}{2}\right)\left(b - \frac{x}{2}\right)} = K = 3{\cdot}5 \times 10^{-3},$$

or, solving the quadratic equation for x,

$$x = -\frac{K(a+b)}{4-K} + \sqrt{\frac{K^2(a+b)^2}{(4-K)^2} + \frac{4abK}{4-K}},$$

and since K is small compared with 4, we may take, with sufficient approximation,

$$x = \sqrt{Kab} - \frac{K(a+b)}{4}.$$

We get, therefore,

(1) for air, where $a = 20{\cdot}8$, and $b = 79{\cdot}2$,
$x_1 = 2{\cdot}4 - 0{\cdot}09 = 2{\cdot}3$ per cent.

(2) for $a = 40$ per cent., and $b = 60$ per cent.
$x_2 = 2{\cdot}8$ per cent.

(3) for $a = 80$ per cent., and $b = 20$ per cent.
$x_3 = 2{\cdot}3$ per cent.

PROBLEM 170 (cf. preceding problem).—What must be the initial composition of the mixture of O_2 and N_2 to give the maximum yield of NO?

SOLUTION 170.—The yield of NO is

$$x = \sqrt{Kab} - \frac{K(a+b)}{4},$$

or, since $a + b = 100$ in mixtures which consist of oxygen and nitrogen only,

$$x = \sqrt{Ka(100-a)} - K \times 25.$$

To obtain the particular concentration a for which x is a maximum, we must differentiate x with respect to a, and put the differential coefficient = 0 :

$$\frac{dx}{da} = \frac{1}{2\sqrt{Ka(100-a)}} \times K(100 - 2a).$$

This expression becomes = 0 when $a = 50$ per cent.

The yield is therefore greatest in a mixture of equal volumes of oxygen and nitrogen.

PROBLEM 171.—On rapidly heating solid ammonium iodide to $t = 357°$ C. a vapour-pressure $P = 275$ mm. is produced, which, owing to the almost complete dissociation of the ammonium iodide, is practically entirely made up of the partial pressures of the dissociation-products HI and NH_3. On keeping the system at this temperature for some time, the vapour-pressure increases, because the hydriodic acid dissociates according to the equation

$$2\,HI = H_2 + I_2.$$

What is the value of the vapour-pressure P' at complete equilibrium, if the dissociation-constant for the reaction $2\,HI = H_2 + I$ is

$$\frac{(H_2)(I_2)}{(HI)^2} = K = 0{\cdot}015\,?$$

SOLUTION 171.—The total vapour-pressure P is equal to the sum of the partial pressures of the individual molecular species. These partial pressures may, for shortness, be expressed by the chemical symbols enclosed in round brackets. On heating rapidly we get then

$$P = (NH_4I) + (NH_3) + (HI),$$

and at complete equilibrium

$$P' = (NH_4I) + (NH_3) + (HI) + (H_2) + (I_2).$$

Since the dissociation of NH_4I into NH_3 and HI is almost complete, (NH_4I) may be neglected in comparison with (NH_3) and (HI), so that we obtain

$$P = (NH_3) + (HI)$$

and

$$(NH_3) = (HI) = \frac{P}{2}.$$

For the dissociation of NH_4I vapour the mass-action equation

$$(NH_3)(HI) = K'(NH_4I)$$

must always be satisfied. If NH_4I is present as a solid phase, then (NH_4I) is constant for a given temperature, and, therefore,

$$(NH_3)(HI) = K'' = \frac{P^2}{4}.$$

The dissociation of HI into H_2 and I_2 takes place according to the equation

$$2\,HI = H_2 + I_2.$$

At complete equilibrium, reached after heating for some time, the following equations must, therefore, be satisfied :—

$$(1)\ (NH_3) = (HI) + \frac{(H_2) + (I_2)}{2},$$

$$(2)\ (H_2) = (I_2),$$

$$(3)\ (NH_3)(HI) = \frac{P^2}{4},$$

$$(4)\ \frac{(H_2)(I_2)}{(HI)^2} = K,$$

$$(5)\ P' = (NH_3) + (HI) + (H_2) + (I_2).$$

In these five equations the five magnitudes P', (NH_3), (HI), (I_2) and (H_2) are unknown. All the unknowns have, therefore, to be calculated.

By eliminating (I_2) by means of equation (2) we obtain

$$(6)\ \text{from (1)}: (NH_3) = (HI) + (H_2),$$

$$(7)\ \text{from (4)}: (H_2) = (HI)\sqrt{K},$$

$$(8)\ \text{from (5)}: P' = (NH_3) + (HI) + 2(H_2).$$

By eliminating (H_2) by means of equation (7) we obtain

$$(9)\ \text{from (6) and (7)}: (NH_3) = (HI)(1 + \sqrt{K}),$$

$$(10)\ \text{from (8) and (7)}: P' = (NH_3) + (HI)(1 + 2\sqrt{K})$$

(3) divided by (9) gives

$$(11)\ (HI)^2 = \frac{P^2}{4(1 + \sqrt{K})}, \text{ or } (HI) = \frac{P}{2} \times \frac{1}{\sqrt{1 + \sqrt{K}}}.$$

From (11) and (9) we obtain

$$(12)\ (NH_3) = \frac{P}{2}\sqrt{1 + \sqrt{K}}.$$

By substituting in equation (10) the values of (HI) and (NH_3) obtained in (11) and (12), we obtain

$$P' = \frac{P}{2}\sqrt{1 + \sqrt{K}} + \frac{P}{2}\frac{1}{\sqrt{1 + \sqrt{K}}}(1 + 2\sqrt{K}),$$

$$= \frac{P}{2}\frac{(2 + 3\sqrt{K})}{\sqrt{1 + \sqrt{K}}}.$$

With $P = 275$ mm. Hg.

$$P' = 137{\cdot}5 \times \frac{2 + 3 \times 0{\cdot}123}{1{\cdot}06} = 307 \text{ mm.}$$

PROBLEM 172.—Iron and water vapour react according to the equation

$$Fe + H_2O = FeO + H_2$$

until a certain state of equilibrium is reached. At $t_1 = 1025°$ C., and under a total pressure of 1 atmosphere, the partial pressure of the hydrogen at equilibrium is $p_{H2} = 427$ mm. Hg, and the partial pressure of the water vapour $p_{H2O} = 333$ mm. At $t_2 = 900°$ C. the corresponding partial pressures are $p'_{H2} = 450$ mm., and $p'_{H2O} = 310$ mm. What is the value of p_{O2}, the dissociation-pressure of ferrous oxide produced by its dissociation into metallic iron and oxygen, at the temperature $T_3 = 1000°$ abs., if the percentage dissociation of pure water vapour at this temperature, and under a pressure $P = 0{\cdot}1$ atmosphere, is $6{\cdot}46 \times 10^{-5}$?

SOLUTION 172.—In the reaction between iron and steam according to the equation

$$Fe + H_2O = FeO + H_2,$$

we have at equilibrium, according to the law of mass-action,

$$(1)\quad \frac{p_{H2}}{p_{H2O}} = K,$$

where the value of K depends on the temperature only. From the data given in the problem K can be calculated for the temperatures $T_1 = 273 + t_1$ and $T_2 = 273 + t_2$.

We must assume that ferrous oxide is dissociated to a definite, though small, extent, according to the equation

$$2\,FeO = 2\,Fe + O_2.$$

the degree of dissociation depending on the temperature. For every temperature, therefore, the partial pressure of the free oxygen p_{O2}, has a definite value. This free oxygen can react with the free hydrogen to form water vapour according to the equation

$$O_2 + 2H_2 = 2H_2O.$$

For this reaction we have at equilibrium,

$$(2)\quad \frac{p^2_{H2O}}{p_{O2} \times p^2_{H2}} = K'.$$

From (1) and (2) we obtain

$$p_{O2} = \frac{1}{K^2K'}.$$

For every temperature for which K and K' are known we can, therefore, calculate p_{O_2}.

K is known for the temperatures T_1 and T_2, and K' for the temperature T_3 can be calculated from the dissociation of water vapour at that temperature. In order to calculate p_{O_2} for T_3, K for T_3 must, therefore, first be found. This can be done by calculating the heat of reaction, Q, for the reaction

$$Fe + H_2O = FeO + H_2$$

by means of van't Hoff's equation

$$\frac{d \log_e K}{dT} = - \frac{Q}{RT^2}.$$

Integrating between the neighbouring temperatures T_1 and T_2 we obtain

$$\log_e \frac{K_1}{K_2} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

and, therefore,

$$(3)\quad Q = \frac{RT_1T_2 \log_e \frac{K_1}{K_2}}{T_2 - T_1}.$$

For the temperature interval $T_3 - T_2$ we obtain similarly

$$(4)\quad Q = \frac{RT_2T_3 \log_e \frac{K_2}{K_3}}{T_3 - T_2}$$

and from (3) and (4)

$$\frac{T_1(T_3 - T_2)}{T_3(T_2 - T_1)}(\log_e K_1 - \log_e K_2) = \log_e K_2 - \log_e K_3.$$

Hence

$$\log_e K_3 = \log_e K_2 - \frac{T_1(T_2 - T_3)}{T_3(T_2 - T_1)}(\log_e K_1 - \log_e K_2),$$

or, converting to common logarithms, and substituting the numerical values,

$$\log K_3 = \log \frac{450}{310} - \frac{1298}{1000} \times \frac{173}{125}\left(\log \frac{427}{333} - \log \frac{450}{310}\right),$$
$$= + 0{\cdot}258.$$

Therefore $K_3 = 1{\cdot}81$.

From the fact that water vapour under a pressure $P = 0{\cdot}1$

atmosphere is dissociated to the extent of $6{\cdot}46 \times 10^{-5}$ per cent. at T_3, the equilibrium-constant K' for the dissociation of water vapour at T_3 may be calculated. The degree of dissociation $a = 6{\cdot}46 \times 10^{-7}$, and, since 1 molecule H_2O gives 1 molecule H_2 and $\frac{1}{2}$ molecule O_2, we have

$$p_{H_2} = aP,\ p_{O_2} = \tfrac{1}{2}aP \text{ and } p_{H_2O} = (1 - a)\,P.$$

Hence

$$K' = \frac{P^2(1 - a)^2}{a^2P^2 \times \frac{1}{2}aP} = \frac{2(1 - a)^2}{a^3P} = \frac{2}{a^3P},$$

since a is very small, compared with 1. If P is expressed in mm. of Hg as above, we obtain, therefore,

$$K' = \frac{2}{(6{\cdot}46)^3 \times 10^{-21} \times 76} = 1 \times 10^{17},$$

and

$$p_{O_2} = \frac{1}{K^2K'} = \frac{1}{(1{\cdot}81)^2 \times 10^{17}} = 3{\cdot}1 \times 10^{-18} \text{ mm.}$$

Problem 173 (cf. preceding problem).—What is the affinity, in calories, at $T_3 = 1000°$ of iron to oxygen under a pressure equal to its partial pressure in the atmosphere, and at what temperature T_x would ferrous oxide, heated in contact with air, dissociate into metallic iron and oxygen, if the molecular heat of formation of ferrous oxide is 64600 calories, and is assumed to be independent of the temperature?

Solution 173.—The affinity of iron to the oxygen of the air is measured by the work which can be gained by the reversible union of one molecule of gaseous oxygen at a pressure of 1/5 atmosphere with metallic iron. For the reaction

$$2\ Fe + O_2 = 2\ FeO$$

the equilibrium-constant at $T_3°$ is $K = 1/p_{O_2}$, where p_{O_2} is the oxygen dissociation-pressure of ferrous oxide at T_3.

From equation (14), therefore, at T_3

$$\begin{aligned} A &= RT_3 \log_e 1/p_{O_2} + RT_3 \log_e 1/5 \\ &= RT_3 \log_e 1/5 - RT_3 \log_e p_{O_2}. \end{aligned}$$

From Problem 172, for $T_3 = 1000°$, $p_{O_2} = 3{\cdot}1 \times 10^{-18}$ mm.

$$= \frac{3{\cdot}1 \times 10^{-18}}{760} = 4{\cdot}1 \times 10^{-21} \text{ atmosphere.}$$

Therefore,

$$\mathbf{A} = 2{\cdot}3 \times 1{\cdot}985 \times 1000\,(\log 1/5 - \log 4{\cdot}1 \times 10^{-21})$$
$$= 2{\cdot}3 \times 1{\cdot}985 \times 1000 \times 19{\cdot}7$$
$$= \mathbf{90000}\text{ calories.}$$

The relation between the dissociation-pressure of ferrous oxide and the temperature is given by the equation

$$\frac{d \log_e p}{dT} = \frac{-Q}{RT^2},$$

or, integrated between T_3 and T_x

$$\log \frac{p_3}{p_x} = \frac{Q}{R}\left(\frac{1}{T_3} - \frac{1}{T_x}\right),$$

where p_3 and p_x are the dissociation-pressures at T_3 and T_x respectively. Q is the heat of dissociation of 2 molecules of FeO, i.e. the heat of the reaction which involves the formation of one molecule of oxygen from 2 molecules of FeO, and therefore, $= -129200$ calories. If T_x is the temperature at which $p_x = 1/5$ atmosphere, then

$$\log \frac{4{\cdot}1 \times 10^{-21}}{1/5} = -\frac{129200}{2{\cdot}3 \times 1{\cdot}98}\left(\frac{1}{1000} - \frac{1}{T_x}\right),$$

and

$$\frac{1}{T_x} = \frac{1}{1000} + \frac{2{\cdot}3 \times 1{\cdot}98}{129200} \times \log (2{\cdot}05 \times 10^{-20})$$
$$= 0{\cdot}001 - 0{\cdot}000696 = 0{\cdot}000304,$$

$\therefore \mathbf{T_x = 3290^\circ}$ abs.

Problem 174 (using the results of the two preceding problems).—Iron and carbon dioxide react according to the equation

$$Fe + CO_2 = FeO + CO.$$

At 1000° abs., and under a total pressure of 1 atmosphere the partial pressure of the carbon dioxide at equilibrium is $p_{CO_2} = 495$ mm. Hg, and that of the carbon monoxide $p_{CO} = 265$ mm. What is the degree of dissociation of pure carbon dioxide (into carbon monoxide and oxygen) at this temperature and under the pressures $P_1 = 0{\cdot}1$, $P_2 = 1$ and $P_3 = 10$ atmospheres ?

Solution 174.—For the dissociation of carbon dioxide into carbon monoxide and oxygen according to the equation

$$2CO_2 = 2CO + O_2,$$

the law of mass-action gives the equilibrium equation

$$(1)\quad \frac{p^2_{CO} \times p_{O_2}}{p^2_{CO_2}} = K.$$

If the carbon monoxide and carbon dioxide are in equilibrium, not only with the free oxygen but also with metallic iron and solid FeO according to the equation

$$Fe + CO_2 = FeO + CO,$$

the equilibrium equation

$$(2)\quad \frac{p_{CO}}{p_{CO_2}} = K.$$

must also be satisfied.

Finally, the equilibrium-pressure of the free oxygen is equal to the dissociation-pressure of FeO at the temperature in question (cf. Problem 173). From (2) and (1) we obtain for the dissociation-constant of carbon dioxide

$$K' = p_{O_2} K^2.$$

For $T = 1000°$ abs.

$$p_{O_2} = 4{\cdot}1 \times 10^{-21} \text{ atmosphere,}$$

$$\text{and } K = \frac{265}{495} = 0{\cdot}535,$$

therefore,

$$K' = 4{\cdot}1 \times 10^{-21} \times (0{\cdot}535)^2 = 1{\cdot}17 \times 10^{-21}.$$

From this value the degree of dissociation a of carbon dioxide under the pressure P may be calculated, since

$$p_{CO_2} = (1 - a)P,\ p_{CO} = aP \text{ and } p_{O_2} = \frac{aP}{2}.$$

From (1) we obtain

$$\frac{a^3P^2 \times \frac{aP}{2}}{(1 - a)^2P^2} = K',$$

$$\text{or } \frac{a^3P}{2(1 - a)^2} = K'.$$

Since the value of K' is very small, a must be small compared with 1 for all but very small values of P; hence

$$a = \sqrt[3]{\frac{2K}{P}},$$

and, for $P_1 = 0{\cdot}1$ atmosphere,

$$a_1 = \sqrt[3]{20 \times 1{\cdot}17 \times 10^{-21}} = 2{\cdot}86 \times 10^{-7},$$

for $P_2 = 1$ atmosphere,

$$a_2 = \sqrt[3]{2 \times 1{\cdot}17 \times 10^{-21}} = 1{\cdot}33 \times 10^{-7},$$

for $P_3 = 10$ atmospheres,

$$a_3 = \sqrt[3]{200 \times 1{\cdot}17 \times 10^{-24}} = 0{\cdot}616 \times 10^{-7}.$$

PROBLEM 175 (cf. preceding problem).—Carbon monoxide and water vapour react to form water-gas, that is, a mixture of these two gases with their reaction products, hydrogen and carbon dioxide. What is the composition of this mixture at equilibrium at a temperature of 1000° abs. and under a total pressure (1) of $P_1 = 0{\cdot}1$ atmosphere, and (2) of $P_2 = 10$ atmospheres, if the carbon monoxide and water vapour from which the equilibrium mixture is produced were originally present in equal volumes?

SOLUTION 175.—Water vapour and carbon monoxide react according to the equation

$$H_2O + CO = H_2 + CO_2.$$

The mass-action equation at equilibrium is, therefore,

$$(1)\ \frac{p_{H_2} \cdot p_{CO_2}}{p_{H_2O} \cdot p_{CO}} = K,$$

where p_{H_2} etc. are the partial pressures of the various gases at equilibrium. Since at the same time both water vapour and carbon dioxide are dissociated to a certain extent, the former into H_2 and O_2, and the latter into CO and O_2, the equations

$$(2)\ \frac{p^2_{H_2} \cdot p_{O_2}}{p^2_{H_2O}} = K_1$$

$$\text{and } (3)\ \frac{p^2_{CO} \cdot p_{O_2}}{p^2_{CO_2}} = K_2$$

must also be satisfied.

K_1 and K_2 for 1000° abs. are known from the preceding examples. By dividing (2) by (3) we obtain

$$\frac{p^2_{H_2} \cdot p^2_{CO_2}}{p^2_{H_2O} \cdot p^2_{CO}} = K^2 = \frac{K_1}{K_2},$$

$$\text{or } K = \sqrt{\frac{K_1}{K_2}}$$

From problem 172 the value of K_1 is 1×10^{-17}, if the partial pressures are expressed in mm. Hg, and, from problem 174, $K_2 = 1{\cdot}17 \times 10^{-21}$, if the partial pressures are expressed in atmospheres. To obtain the value of K_1 when the partial pressures are also expressed in atmospheres, 1×10^{-17} must be divided by 760, giving $K_1 = 1{\cdot}24 \times 10^{-20}$.

For the numerical value of K we therefore obtain

$$K = \sqrt{\frac{1{\cdot}24 \times 10^{-20}}{1{\cdot}17 \times 10^{-21}}} = \sqrt{10{\cdot}6} = 3{\cdot}26.$$

The numerical value of K is independent of the arbitrary unit of pressure, because both numerator and denominator of equation (1) are of the same degree with respect to p, or, in other words, because the reaction takes place without change of volume (or pressure).

If the fraction x of unit volume of water originally present is transformed into CO_2 and H_2, which are formed in equal volumes, there will be in the equilibrium-mixture $(1 - x)$ vol. H_2O, x vol. CO_2, x vol. H_2 and, if the initial volumes of CO and H_2O were equal, $(1 - x)$ vol. CO; hence

$$\frac{x^2}{(1-x)^2} = K, \quad \frac{x}{1-x} = \sqrt{K} = 1{\cdot}81,$$
$$\text{and} \quad x = 0{\cdot}644.$$

From a mixture which originally contained 50 % by volume of H_2O and 50 % by volume of CO, there is formed, therefore, an equilibrium-mixture containing

32·2 % CO_2, 32·2 % H_2, 17·8 % CO and 17·8 % H_2O by volume.

Since K is independent of the pressure, the composition of the equilibrium-mixture is also independent of the pressure.

PROBLEM 176 (cf. preceding problem).— The molecular heat of combustion of hydrogen is $Q_1 = 58000$ cals., and that of carbon monoxide is $Q_2 = 68000$ cals. What is the composition at equilibrium of the water-gas formed from equal volumes of water vapour and carbon monoxide (1) at a temperature $T_1 = 800°$ abs., and (2) at a temperature $T_2 = 1200°$ abs.?

SOLUTION 176.—The reaction $H_2O + CO = H_2 + CO_2$ is made up of the two subsidiary reactions

$$(1)\ H_2O = H_2 + \tfrac{1}{2}O_2,$$
$$\text{and } (2)\ \tfrac{1}{2}O_2 + CO = CO_2.$$

The heat of reaction (1) is $Q_1 = -58000$ cals., and of reaction (2) $Q_2 = 68000$ cals. The heat effect of the total reaction $H_2O + CO = H_2 + CO_2$ is, therefore,

$$Q = Q_1 + Q_2 = +10000 \text{ cals.}$$

The equilibrium-constant K changes with temperature according to the equation

$$\frac{d \log_e K}{dT} = \frac{-Q}{RT^2}.$$

Integration between the neighbouring temperatures T and T_1 gives

$$(3) \quad \log_e \frac{K}{K_1} = \frac{+Q}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right),$$

and similarly between the temperatures T and T_2

$$(4) \quad \log_e \frac{K}{K_2} = \frac{+Q}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right).$$

From problem 175, the value of K for $T = 1000°$ abs. is 3·26. K_1 for $T_1 = 800°$ abs. and K_2 for $T_2 = 1200°$ abs. may, therefore, be calculated. From (3) we obtain

$$\log K_1 = \log K - \frac{0{\cdot}4343Q(T_1 - T)}{RTT_1}$$

$$= 0{\cdot}513 + \frac{0{\cdot}4343 \times 10000 \times 200}{1{\cdot}985 \times 1000 \times 800}$$

$$= 0{\cdot}513 + 0{\cdot}552 = 1{\cdot}065,$$

and, therefore, $\mathbf{K_1 = 11{\cdot}6}$.

Similarly, from (4),

$$\log K_2 = \log K - \frac{0{\cdot}4343Q(T_2 - T)}{RTT_2}$$

$$= 0{\cdot}149,$$

and $\mathbf{K_2 = 1{\cdot}41}$.

If x_1 is the fraction of the water vapour transformed at T_1 according to the equation $H_2O + CO = H_2 + CO_2$, and x_2 the corresponding fraction at T_2, then, as in problem 175, we obtain

$$\frac{x_1}{1 - x_1} = \sqrt{K_1} = \sqrt{11{\cdot}6} = 3{\cdot}40,$$

$$x_1 = 0{\cdot}774,$$

$$\text{and } \frac{x_2}{1 - x_2} = \sqrt{K_2} = \sqrt{1{\cdot}41} = 1{\cdot}19,$$

$$x_2 = 0{\cdot}542.$$

The composition of the water-gas mixture is, therefore,

at $T_1 = 800°$ abs.:

38·7 $\%$ CO_2, **38·7** $\%$ H_2, **11·3** $\%$ H_2O, **11·3** $\%$ CO,

and at $T_2 = 1200°$ abs.:

27·1 $\%$ CO_2, **27·1** $\%$ H_2, **22·9** $\%$ H_2O, **22·9** $\%$ CO.

PROBLEM 177.—A mixture of $a = 10\,\%$ by volume of SO_2 and $b = 90\,\%$ by volume of O_2 is passed at the rate of $v = 5$ litres per hour (measured at atmospheric pressure and 20° C.) through a tube filled with a catalytic agent and heated in a furnace to 723° C. In the tube combination to SO_3 takes place, and we shall assume that the gases remain long enough in the tube for the equilibrium between the three gases SO_2, O_2 and SO_3 to be reached, and that the gases leave the tube by a capillary so quickly that the equilibrium is not disturbed. On leaving the capillary the gas passes through a solution of barium chloride, from which it precipitates in $t = 2$ hours $A = 5{\cdot}84$ grams of $BaSO_4$. What is the equilibrium-constant K_p of the reaction $2SO_2 + O_2 = 2SO_3$ at 723° C.?

SOLUTION 177.—Let the fraction x of the SO_2 present in the initial mixture be converted into SO_3 at equilibrium. Then, since for every volume of SO_3 formed one volume of SO_2 and half a volume of O_2 disappears, a volumes of $SO_2 + b$ volumes of oxygen give at equilibrium $a(1 - x)$ volumes of $SO_2 + ax$ volumes of $SO_3 + b - \frac{ax}{2}$ volumes of oxygen. The total volume at equilibrium is, therefore, $a + b - \frac{ax}{2}$. The total volume has, therefore, diminished from $a + b = 100$ to $a + b - \frac{ax}{2} = 100 - \frac{ax}{2}$. Since the total pressure remains constant at one atmosphere, the partial pressures of the three gases at equilibrium are

$$(SO_2) = \frac{a - ax}{100 - \frac{ax}{2}}, (SO_3) = \frac{ax}{100 - \frac{ax}{2}} \text{ and } (O_2) = \frac{b - \frac{ax}{2}}{100 - \frac{ax}{2}}$$

atmospheres, and, therefore,

$$(1)\ K_p = \frac{(SO_3)^2}{(SO_2)^2(O_2)} = \frac{\dfrac{(ax)^2}{\left(100 - \dfrac{ax}{2}\right)^2}}{\dfrac{(a - ax)^2}{\left(100 - \dfrac{ax}{2}\right)^2} \times \dfrac{\left(b - \dfrac{ax}{2}\right)}{\left(100 - \dfrac{ax}{2}\right)}} = \frac{x^2\left(100 - \dfrac{ax}{2}\right)}{(1 - x)^2\left(b - \dfrac{ax}{2}\right)}.$$

x and, therefore, K_p may be calculated as follows: Let n be the number of gram-molecules of a gas which occupy a volume of 1 litre at 20° C. and atmospheric pressure. Then $\frac{nvat}{100}$ gram-molecules of SO_2 enter the furnace in time t. But the fraction x of the SO_2 is converted into SO_3, therefore $\frac{xnvat}{100}$ gram-molecules of SO_3 leave the furnace in time t. These are converted completely into $BaSO_4$ and weighed as such. If M is the molecular weight of $BaSO_4$, there is, therefore, precipitated in time t

$$A = \frac{xnvatM}{100} \text{ grams } BaSO_4,$$

$$\text{and } (2)\ x = \frac{100A}{nvatM}.$$

The equation $PV = nRT$ enables us to calculate n. Here $P = 1$ atmosphere, $V = 1$ litre, $R = 0{\cdot}082$ and $T = (20 + 273) = 293$. Therefore,

$$n = \frac{PV}{RT} = \frac{1 \times 1}{0{\cdot}082 \times 293} = 0{\cdot}0416,$$

and, substituting the numerical values in (2),

$$x = \frac{100 \times 5{\cdot}84}{0{\cdot}0416 \times 5 \times 10 \times 2 \times 233} = 0{\cdot}60.$$

Finally, substituting the numerical values in (1), we obtain

$$K_p = \frac{(0{\cdot}60)^2\left(100 - \dfrac{10 \times 0{\cdot}60}{2}\right)}{(1 - 0{\cdot}60)^2\left(90 - \dfrac{10 \times 0{\cdot}60}{2}\right)} = \frac{0{\cdot}36 \times 97}{0{\cdot}16 \times 87}$$

$$= 2{\cdot}5.$$

Partition Law—Example

PROBLEM 178.—The partition-coefficient of iodine for water and carbon disulphide is $K = 0{\cdot}0017$. An aqueous solution of iodine containing $a = 0{\cdot}1$ gram of iodine per 100 c.c. is shaken with carbon disulphide. To what value does the concentration of the aqueous solution sink (1) when a litre of it is shaken with 50 c.c. of carbon disulphide, (2) when a litre of it is shaken successively with five separate quantities of carbon disulphide of 10 c.c. each?

SOLUTION 178.—(1) Let the concentration of the aqueous solution, after shaking with 50 c.c. of carbon disulphide, be x grams per 100 c.c. Then $10(a - x)$ grams of iodine have been extracted by the carbon disulphide. The concentration of the carbon disulphide solution is, therefore,

$$\frac{10(a - x) \times 100}{50} = 20(a - x)$$

grams iodine per 100 c.c. Hence

$$\frac{x}{20(a - x)} = K,$$

$$x = \frac{20aK}{1 + 20K} = \frac{0{\cdot}0034}{1{\cdot}034} = \mathbf{0{\cdot}00329} \text{ gram per 100 c.c.}$$

(2) Let the concentration of the iodine in the water, after the first extraction with 10 c.c. of carbon disulphide, be x_1 grams per 100 c.c. Then

$$\frac{x_1}{100(a - x_1)} = K,$$

$$x_1 = \frac{100aK}{1 + 100K}.$$

If the concentration of the aqueous solution after the second extraction is x_2, we obtain similarly

$$\frac{x_2}{100(x_1 - x_2)} = K,$$

$$x_2 = \frac{100x_1K}{1 + 100K} = a\left(\frac{100K}{1 + 100K}\right)^2.$$

After the fifth extraction the concentration is, therefore,

$$x_5 = a\left(\frac{100K}{1 + 100K}\right)^5$$

$$= 0{\cdot}1\left(\frac{0{\cdot}17}{1{\cdot}17}\right)^5 = \mathbf{6{\cdot}47 \times 10^{-6}} \text{ gram iodine per 100 c.c.}$$

The extraction has, therefore, been practically complete.

Solubility of Gases—Example

PROBLEM 179.—The solubility-coefficient of oxygen at 0° is $s = 0{\cdot}04$ and of hyrodgen $s' = 0{\cdot}02$. What is the percentage composition by volume of the dissolved gas when a litre of water at 0° is shaken in a closed space with 3 times its volume of electrolytic gas under an initial pressure of 1 atmosphere? What are the final partial pressures p and p' of the oxygen and hydrogen in the gas above the liquid at equilibrium?

SOLUTION 179.—Since $\frac{1}{3}$ of the volume of the electrolytic gas is oxygen, the initial partial pressure of the oxygen in the mixture is $\frac{1}{3}$ atmosphere. Let p be the partial pressure of the oxygen at equilibrium. The volume of oxygen absorbed by the litre of water is

$s = 0{\cdot}04$ litre measured at 0° and p atmos.
$= 0{\cdot}04 \times 3p$ litre ,, ,, ,, $\frac{1}{3}$,,

The oxygen left would occupy a volume of $3 - 0{\cdot}04 \times 3p$ litres at 0° and $\frac{1}{3}$ atmos., but must fill the volume of 3 litres at 0° and p atmos. As the volume is inversely proportional to the pressure, we obtain

$$\frac{3 - 0{\cdot}04 \times 3p}{3} = \frac{p}{\frac{1}{3}} = 3p$$

$$1 - 0{\cdot}04p = 3p,$$

$$\therefore \mathbf{p = 0{\cdot}329} \text{ atmos.}$$

The volume of oxygen absorbed by the water is, therefore,

$= 0{\cdot}04$ litre at 0° and 0·329 atmos.
$= 0{\cdot}04 \times 0{\cdot}329$ litre at 0° and 1 atmos.
$= 0{\cdot}0132$,, ,, ,, 1 ,,

Similarly for hydrogen, the initial partial pressure is 2/3 atmos., and the final partial pressure p' is obtained from the equation

$$\frac{3 - \frac{0{\cdot}02 \times 3p'}{2}}{3} = \frac{p'}{2/3} = \frac{3p'}{2}$$

$$\therefore p' = \mathbf{0{\cdot}662} \text{ atmos.}$$

The volume of hydrogen absorbed is

0·02 litre at 0° and 0·662 atmos.
$= 0{\cdot}02 \times 0{\cdot}662 = 0{\cdot}0132$ litre at 0° and 1 atmos.

The total volume of gas dissolved is, therefore, 0·0132 + 0·0132 = 0·0264 litre at 0° and 1 atmos., and since it consists of equal volumes of hydrogen and oxygen, the percentage composition is

O_2 = 50 per cent., H_2 = 50 per cent.

Problems for Solution

Mass-action—Equilibrium and Temperature—Affinity

PROBLEM 180.—When 2·94 moles of iodine and 8·10 moles of hydrogen are heated at constant volume at 444° till equilibrium is established, 5·64 moles of hydriodic acid are formed. If we start with 5·30 moles of iodine and 7·94 moles of hydrogen, how much hydriodic acid is present at equilibrium at the same temperature?

Ans. 9·49 moles.

PROBLEM 181 (cf. preceding problem).—What proportion of hydriodic acid is decomposed when 1 mole is heated to 444° till equilibrium is established?

Ans. 0·2197 mole.

PROBLEM 182.—When 5·71 moles of iodine and 6·22 moles of hydrogen are heated to 357° till equilibrium is established, 9·55 moles of hydriodic acid are formed. From the equilibrium constants calculated from these data and the data in problem 180, calculate the heat of formation of hydriodic acid from hydrogen and iodine vapour according to the equation

$$H_2 + I_2 = 2HI.$$

Ans. 3028 cals.

PROBLEM 183.—If 1 mole of acetic acid and 1 mole of ethyl alcohol are mixed, the reaction

$$CH_3 . COOH + C_2H_5OH = CH_3 . COOC_2H_5 + H_2O$$

proceeds till equilibrium is reached, when 1/3 mole acetic acid, 1/3 mole ethyl alcohol, 2/3 mole ethyl acetate, and 2/3 mole water are present. If we start (*a*) with 1 mole acid + 2 moles alcohol, (*b*) with 1 mole acid, 1 mole alcohol, and 1 mole water, (*c*) with 1 mole ester + 3 moles water, how much ester is present in each case at equilibrium?

Ans. (*a*) 0·845 mole, (*b*) 0·543 mole, (*c*) 0·465 mole.

PROBLEM 184.—Above 150° NO_2 begins to dissociate according to the equation

$$NO_2 = NO + \tfrac{1}{2}O_2.$$

At 390° the vapour-density of NO_2 is 19·57 (H = 1), and at 490° it is 18·04 Calculate the degree of dissociation according to the above equation at each of these temperatures, the equilibrium-constants $K = \frac{[NO]\,[O_2]^{\frac{1}{2}}}{[NO_2]}$, expressing the concentrations in gram-molecules per litre, and the heat of dissociation of NO_2.

Ans. $a_1 = 0{\cdot}35$, $a_2 = 0{\cdot}55$. $K_1 = 2{\cdot}818 \times 10^{-2}$, $K_2 = 7{\cdot}716 \times 10^{-2}$. $Q = -9376$ cals.

PROBLEM 185.—At 49·7° C., and under a total pressure of 261·4 mm. of mercury, N_2O_4 is 63 per cent. dissociated into NO_2. What would be its degree of dissociation at the same temperature, but under a pressure of 93·8 mm.?

Ans. 80·4 per cent.

PROBLEM 186.—What is the equilibrium-constant at 49·7° for the above dissociation, (*a*) for partial pressures in mm., (*b*) for partial pressures in atmospheres, (*c*) for concentrations in gram-molecules per litre, (*d*) for concentrations in grams per litre?

Ans. (*a*) 172, (*b*) 172/760, (*c*) 0·00855, (*d*) 0·1966,

or 4 times these numbers, according to the expression used for the equilibrium-constant. See problem 166.

PROBLEM 187.—The vapour-pressure of solid NH_4HS at 25·1° is 50·1 cms. Assuming that the vapour is practically completely dissociated into NH_3 and H_2S, calculate the total pressure at equilibrium when solid NH_4HS is allowed to dissociate at 25·1° in a vessel containing NH_3 at a pressure of 32 cms.

Ans. 59·5 cms.

PROBLEM 188.—What is the total pressure in the preceding problem when the vessel contains H_2S at a pressure of 32 cms. instead of NH_3?

Ans. 59·5 cms.

PROBLEM 189.—In the reaction

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

there is equilibrium at 200° when the partial pressure of steam is 4·6 cms., and that of H_2 is 95·9 cms. What is the pressure of H_2 at equilibrium when that of steam is 9·7 cms.?

Ans. 202·2 cms.

PROBLEM 190 (cf. preceding problem).—Iron is heated at 200° in a closed vessel with steam at an initial pressure of 1 atmosphere till equilibrium is established. What are the partial pressures of steam and hydrogen at equilibrium?

Ans. H_2O = 0·0458 atmos., H_2 = 0·954 atmos.

PROBLEM 191 (cf. preceding problem).—If the capacity of the vessel in the preceding problem is 2 litres, what weight of Fe_3O_4 is formed at equilibrium?

Ans. 2·85 grams.

PROBLEM 192.—Amylene and trichloracetic acid react to form an ester according to the equation

$$CCl_3 . COOH + C_5H_{10} = CCl_3 . COOC_5H_{11}.$$

In an experiment at 100° the equilibrium mixture contained 3·846 gram-molecules amylene per litre, 0·6594 gram-molecule acid per litre, and 2·111 gram-molecules ester per litre. If we start with 1 gram-molecule acid, and 4·48 gram-molecules amylene in 638 c.c. at 100°, what is the composition of the mixture at equilibrium?

Ans. 0·174 gram-molecule acid, 3·654 gram-molecules amylene, and 0·826 gram-molecule ester in 638 c.c.

PROBLEM 193.—Solid NH_4CN has a considerable vapour-pressure at ordinary temperatures, and the vapour is practically completely dissociated into NH_3 and HCN. At 11° C. the total vapour-pressure is 22·7 cms. of mercury. (*a*) What will be the partial pressure of HCN if solid NH_4CN is allowed to sublime at 11° in a closed vessel filled with NH_3 at a pressure of 32·28 cms. of mercury? (*b*) What will be the final total pressure?

Ans. (*a*) 3·595 cms. Hg, (*b*) 39·47 cms. Hg.

PROBLEM 194.—If the volume of the vessel in the preceding problem is 1 litre, how much NH_4CN will sublime?

Ans. 0·00203 gram-molecule.

PROBLEM 195.—At 96° the ammonia dissociation-pressure of the compound $LiCl . NH_3$ according to the equation

$$LiCl . NH_3 = LiCl + NH_3$$

is 367 mm. of mercury, and at 109·2° it is 646 mm. Calculate the heat of dissociation of the compound.

Ans. – 12000 cals.

PROBLEM 196.—At 2000° C., and under atmospheric pressure, carbon dioxide is 1·80 per cent. dissociated according to the equation

$$2CO_2 = 2CO + O_2.$$

Calculate the equilibrium-constant for the above reaction using partial pressures (in atmospheres).

Ans. 3×10^{-6}.

PROBLEM 197.—What is the equilibrium-constant in the preceding problem, if the concentrations are expressed in gram-molecules per litre?

Ans. $1{\cdot}61 \times 10^{-8}$.

PROBLEM 198.—At 28·85° the vapour-pressure of the system $BaCl_2$, $2H_2O$ – $BaCl_2$, H_2O is 7·125 mm., and at 31·65° it is 8·945 mm. Calculate the heat of hydration of $BaCl_2$, H_2O to $BaCl_2$, $2H_2O$ by water vapour.

Ans. 14910 cals.

PROBLEM 199.—At 30·20° the vapour-pressure of the system $CuSO_4$, $5H_2O$ – $CuSO_4$, $3H_2O$ is 10·90 mm., and at 26·30° it is 8·074 mm. Calculate the heat of hydration of $CuSO_4$, $3H_2O$ to $CuSO_4$, $5H_2O$ by water vapour per gram-molecule water.

Ans. 13940 cals.

PROBLEM 200 (cf. preceding problem).—At 30·20° and 26·30° the vapour-pressure of water is 31·93 mm. and 25·43 mm. respectively. Calculate the heat of hydration of $CuSO_4$, $3H_2O$ to $CuSO_4$, $5H_2O$ by liquid water per gram-molecule water.

Ans. 3382 cals.

PROBLEM 201.—The solubility of boric acid in water is 38·45 grams per litre at 13°, and 49·09 grams per litre at 20°. Calculate the heat of solution of boric acid per gram-molecule.

Ans. – 5840 cals.

PROBLEM 202.—The solubility of succinic acid at 0° is 2·88 gram-molecules per litre and at 8·5° it is 4·22 gram-molecules per litre. Calculate the heat of solution of succinic acid per gram-molecule.

Ans. – 6900 cals.

PROBLEM 203.—The dissociation-pressure of $CaCO_3$ at 810° C. is 678 mm. and at 865° C. it is 1333 mm. Calculate the heat of dissociation of $CaCO_3$.

Ans. − 30110 cals.

PROBLEM 204 (cf. preceding problem).—At what temperature does the dissociation-pressure of $CaCO_3$ become equal to 1 atmosphere.

Ans. 818° C.

PROBLEM 205 (cf. preceding problem). — What is the affinity of CaO to CO_2 at atmospheric pressure at a temperature of 810° C.?

Ans. 246 cals.

PROBLEM 206.—At 10° the solubility of $HgCl_2$ is 6·57 grams per 100 c.c. and at 50° 11·84 grams per 100 c.c. Calculate the heat of solution per gram-molecule.

Ans. − 2669 cals.

PROBLEM 207.—At 10° the electrolytic dissociation-constants of acetic and butyric acids are $1{\cdot}79 \times 10^{-5}$ and $1{\cdot}66 \times 10^{-5}$ respectively, and at 40° they are $1{\cdot}87 \times 10^{-5}$ and $1{\cdot}62 \times 10^{-5}$. Calculate the heat of ionisation at 25° (*a*) of acetic, (*b*) of butyric acid.

Ans. (*a*) − 256·6 cals., (*b*) 144 cals.

PROBLEM 208. — At 10° the ionic product of water is $0{\cdot}314 \times 10^{-14}$ and at 34° $2{\cdot}16 \times 10^{-14}$. Calculate the heat of formation of H_2O from H and OH′.

Ans. 13950 cals.

PROBLEM 209.—At 25° the degree of dissociation of *o*-chlorbenzoic acid at a dilution of 512 litres is 0·557 as measured by the conductivity; at 40° and at the same dilution it is 0·521. Calculate the heat of dissociation of the acid at 32·5°.

Ans. 2614 cals.

PROBLEM 210.—At 20° the solubility of AgBr is $4{\cdot}5 \times 10^{-7}$ gram-molecule per litre and at 25° it is $7{\cdot}3 \times 10^{-7}$. What is the heat of precipitation of AgBr?

Ans. 16880 cals.

PROBLEM 211.—At 20° the solubility of AgCl is $1{\cdot}1 \times 10^{-5}$ gram-molecule per litre and the heat of precipitation of AgCl is 16000 cals. What is the solubility of AgCl at 30°?

Ans. $1{\cdot}73 \times 10^{-5}$ gram-mol./litre

PROBLEM 212.—At 670° C. the oxygen dissociation-pressure of BaO_2 is 80 mm. and at 720° C. 210 mm. (*a*) What is the heat of the reaction $2BaO_2 = 2BaO + O_2$? (*b*) At what temperature is the dissociation-pressure equal to the partial pressure of oxygen in the atmosphere (152 mm.)?

Ans. (*a*) − 36090 cals., (*b*) 703° C.

PROBLEM 213 (cf. preceding problem).—What is the maximum work obtainable at 670° C. by the formation of 2 gram-molecules of BaO_2 from BaO and oxygen at the pressure at which it occurs in the atmosphere?

Ans. 1203 cals.

PROBLEM 214.—At 2000° C. the equilibrium-constant for pressures in atmospheres for the reaction $CO + \frac{1}{2}O_2 = CO_2$ is $1{\cdot}07 \times 10^2$. What is the maximum work obtainable by the formation at 2000° C. of 1 gram-molecule of CO_2 at atmospheric pressure from 1 gram-molecule of CO and $\frac{1}{2}$ gram-molecule of O_2, both at atmospheric pressure?

Ans. 21210 cals.

Partition Law

PROBLEM 215.—At 15° an aqueous solution of succinic acid containing 0·070 gram in 10 c.c. is in equilibrium with an ethereal solution containing 0·013 gram in 10 c.c. Succinic acid has its normal molecular weight in both water and ether. What is the concentration of an ethereal solution which is in equilibrium with an aqueous solution containing 0·024 gram in 10 c.c.?

Ans. 0·0044 gram in 10 c.c.

PROBLEM 216.—At 25° a solution of iodine in water containing 0·0516 gram per litre is in equilibrium with a CCl_4 solution containing 4·412 grams iodine per litre. The solubility of iodine in water at 25° is 0·340 gram per litre. What is the solubility in CCl_4?

Ans. 29·07 grams per litre.

PROBLEM 217.—In the partition of acetic acid between CCl_4 and water, the concentration of the acetic acid in the CCl_4 layer was *C* gram-mols. per litre and in the corresponding water layer *W* gram-mols. per litre.

C	0·292	0·363	0·725	1·07	1·41
W	4·87	5·42	7·98	9·69	10·7

Acetic acid has its normal molecular weight in aqueous solution. From these figures show that, at these concentrations, the acetic acid in the CCl_4 solution exists as double molecules.

PROBLEM 218.—In the partition of succinic acid between water and ether the concentrations of the acid in the water and ether layers were c_1 and c_2 respectively.

c_1	0·121	0·070	0·024	gram in 10 c.c.
c_2	0·022	0·013	0·0046	,, ,,

In the distribution of the same substance between water and benzene the concentrations of the acid in the water and benzene layers were c_3 and c_4 respectively.

c_3	0·0150	0·0195	0·0289	gram in 10 c.c.
c_4	0·242	0·412	0·970	,, ,,

Succinic acid has its normal molecular weight in water. What is its molecular weight (*a*) in ether, (*b*) in benzene?

Ans. (*a*) 118, (*b*) 236.

PROBLEM 219.—Phenol has its normal molecular weight in both water and amyl alcohol. At 25° an amyl alcohol solution containing 10·53 grams phenol per litre is in equilibrium with an aqueous solution containing 0·658 gram per litre. What weight of phenol is extracted from 500 c.c. of an aqueous solution containing 0·4 gram-mols. phenol per litre by shaking it twice with amyl alcohol, using 100 c.c. each time?

Ans. 17·7 grams.

PROBLEM 220.—The partition-coefficient of iodine for CS_2/water is 410. A solution of KI containing 8 grams per litre was shaken with iodine and CS_2 till equilibrium was established. The concentration of the iodine in the two layers was then determined by titration with $Na_2S_2O_3$. The aqueous layer contained 2·15 grams iodine per litre and the CS_2 layer 35·42 grams per litre. Assuming that in the aqueous solution KI reacts with iodine according to the equation $KI + I_2 = KI_3$, calculate the dissociation-constant of the tri-iodide, $K = [KI][I_2]/[KI_3]$, expressing the concentrations in gram-mols. per litre. (The concentration of the I_2 in the aqueous layer obtained by titration is the sum of the free I_2 and the I_2 combined with KI in the tri-iodide. KI and KI_3 are assumed insoluble in CS_2.)

Ans. $K = 1{\cdot}68 \times 10^{-3}$.

PROBLEM 221.—In aqueous solution benzoic acid exists

as single molecules, partly electrolytically dissociated. In benzene solution it exists partly as single and partly as double molecules, the proportions depending on the concentration. Taking the partition-coefficient water/benzene for the single molecules = 0·700, calculate from the following data the equilibrium-constant for the dissociation of the double molecules into single molecules in the benzene solution according to the equation

$$(C_6H_5COOH)_2 = 2C_6H_5 . COOH.$$

At 10° the concentration of benzoic acid in the water layer = 0·0429 gram per 200 c.c. and the degree of electrolytic dissociation = 0·169. In the benzene layer the concentration of benzoic acid = 0·1449 gram per 200 c.c. Express concentrations in grams per litre.

Ans. $K = 0·138$.

Solubility of Gases

PROBLEM 222.—The solubility-coefficient of oxygen in water at 0° is 0·04, and of nitrogen 0·02. If the composition of air by volume is assumed to be 21 per cent. oxygen and 79 per cent. nitrogen, what is the percentage composition by volume of the gas expelled by boiling from water which has been saturated by free exposure to air at 0°?

Ans. 34·7 per cent. O_2, 65·3 per cent. N_2.

PROBLEM 223 (cf. preceding problem).—If the composition of the air were O_2 = 20·6 per cent., N_2 = 79 per cent., CO_2 = 0·4 per cent. by volume, and the solubility-coefficient of CO_2 1·79 at 0°, what would be the percentage composition of the dissolved gas?

Ans. O_2 = 26·40 per cent., N_2 = 50·64 per cent.,
CO_2 = 22·95 per cent.

PROBLEM 224.—1 litre of oxygen-free water is shaken in a closed space at 0° with 1 litre of oxygen at an initial pressure of 1 atmosphere. (*a*) What volume of oxygen, measured at 0° and 760 mm., dissolves, and (*b*) what is the pressure of the oxygen over the water when equilibrium is established?

Ans. (*a*) 38·5 c.c., (*b*) 0·9615 atmos.

PROBLEM 225 (cf. preceding problem).—1 litre of oxygen is shaken with 10 litres of water at 0° in a closed vessel.

The initial pressure of the oxygen is 1 atmosphere. (*a*) What volume of oxygen (at 0° and 760 mm.) dissolves, and (*b*) what is the final pressure of the undissolved oxygen?

Ans. (*a*) 285·6 c.c., (*b*) 0·714 atmos.

PROBLEM 226.—What is the percentage composition by volume of the gas dissolved when a gas mixture containing 21 per cent. O_2 and 79 per cent. N_2 by volume, and under an initial total pressure of 1 atmosphere, is shaken in a closed vessel at 0° (*a*) with an equal volume of water, (*b*) with 10 times its volume of water?

Ans. (*a*) 34·18 per cent. O_2, 65·83 per cent. N_2.

(*b*) 31·42 per cent. O_2, 68·58 per cent. N_2.

PROBLEM 227.—The solubility-coefficient of CO_2 at 0° is 1·8. What weight of CO_2 under a pressure of 4 atmospheres will dissolve in a litre of water at 0°?

Ans. 14·1 grams.

PROBLEM 228.—What is the relation between the solubility-coefficient s of a gas at $t°$ and the absorption-coefficient a of the gas?

Ans. $s = \frac{a(273 + t)}{273}$.

CHAPTER IX

OHM'S LAW.—HEATING EFFECT OF CURRENT.—FARADAY'S LAWS.—SPECIFIC, EQUIVALENT, AND MOLECULAR CONDUCTIVITY OF ELECTROLYTES.—DEGREE OF DISSOCIATION.—DISSOCIATION-CONSTANT.—TRANSPORT NUMBERS.—SOLUBILITY-PRODUCT.—HYDROLYSIS

Ohm's Law

ACCORDING to Ohm's law, the current C produced in a conductor of resistance R by the potential difference E between the ends of the conductor is

$$(1)\quad C = \frac{E}{R}.$$

If E is measured in volts, and R in ohms, C is obtained in amperes.

Quantity of Electricity

If a current of C amperes flows through a conductor, the quantity of electricity which passes any cross-section of the conductor in t seconds is

$$(2)\quad W = Ct \text{ coulombs.}$$

Heating Effect of Current

The current C amperes flowing through the resistance R ohms for t seconds, under the potential difference E volts, develops the quantity of energy

$$(3)\quad Q = WE = CEt = C^2Rt \text{ volt-coulombs or joules}$$
$$= 0{\cdot}239 \times C^2Rt \text{ calories}$$

since 1 joule = 0·239 calorie.

Faraday's Laws

Faraday's laws state that the quantity of an electrolyte decomposed by an electric current is proportional to the quantity

of electricity which passes any cross-section of the electrolyte, and that the quantities of different electrolytes decomposed by the same quantity of electricity are proportional to their chemical equivalents. These statements may be summed up as follows. The quantity of electricity, 96540 coulombs, is required for the decomposition of 1 gram-equivalent of any electrolyte, or for the liberation of 1 gram-equivalent of any cation or anion. The quantity of electricity, 96540 coulombs, is called one faraday, and is usually denoted by the symbol F.

Heating Effect—Examples

PROBLEM 229.—A thermostat of $v = 850$ litres capacity is kept at a constant temperature of 25° C. by the heat developed by maintaining a current of $C = 3{\cdot}1$ amp. through a resistance of $R = 22$ ohms placed in the thermostat. How many degrees does the temperature of the thermostat fall in $t = 30$ minutes, after switching off the heating current?

SOLUTION 229.—If the thermostat maintains a constant temperature, the quantity of heat given up to the surroundings at any instant by evaporation of water, conduction and radiation of heat, must be equal to the quantity supplied by the heating current.

The quantity of heat supplied by the heating current can be calculated from the data given in the problem. According to formula (3), the heat developed by the current in 1 second ($t = 1$) is $0{\cdot}239\ C^2R$ calories. If the heating current is switched off, the thermostat, therefore, gives up $0{\cdot}239\ C^2R$ calories per second, and in t minutes $60 \times 0{\cdot}239\ C^2Rt$ calories. If the thermostat contains v litres of water (specific heat = 1), in t minutes the temperature, therefore, falls

$$t^\circ = \frac{60 \times 0{\cdot}239 \times C^2Rt}{1000\ v} = \frac{60 \times 0{\cdot}239 \times (3{\cdot}1)^2 \times 22 \times 30}{1000 \times 850}$$

$$= 0{\cdot}107^\circ\ C.$$

PROBLEM 230.—For the production of the heating current in the previous problem only a potential of 220 volts is available. A lamp-resistance is to be used for the necessary current-regulation. How many lamps (in parallel) are required (1) if each lamp has a resistance of $R_1 = 1000$ ohms? (2) if each lamp has a resistance of $R_2 = 300$ ohms?

SOLUTION 230.—According to Ohm's law (1), $C = \frac{E}{R}$. If, therefore, the only resistance in the circuit were the heating-resistance $R = 22$ ohms, the current would be $\frac{220}{22} = 10$ amps. In order that the current in the circuit may be $C = 3{\cdot}1$ amps., the resistance must be increased to $\frac{220}{3{\cdot}1} = 71$ ohms. An additional resistance of $71 - 22 = 49$ ohms, in series with the heating-resistance is, therefore, required. This additional resistance is to take the form of glow-lamps arranged in parallel.

(1) In the first case the resistance of each lamp is R_1 ohms. If n_1 such lamps are arranged in parallel their total resistance is $\frac{R_1}{n_1}$ ohms, and this must be = 49 ohms,

$$\therefore n_1 = \frac{R_1}{49} = \frac{1000}{49}.$$

(2) In the second case the resistance of each lamp is R_2 ohms. The total resistance of n_2 such lamps in parallel is $\frac{R_2}{n_2}$ ohms, which must also be equal to 49 ohms, the additional resistance required,

$$\therefore n_2 = \frac{R_2}{49} = \frac{300}{49}.$$

Since n_1 and n_2 must be whole numbers, the necessary conditions are very approximately fulfilled by

$$\mathbf{n_1 = 20 \text{ and } n_2 = 6.}$$

In the first case the current is

$$C_1 = \frac{220}{22 + \frac{1000}{20}} = 3{\cdot}06 \text{ amps.}$$

and in the second case

$$C_2 = \frac{220}{22 + \frac{300}{6}} = 3{\cdot}06 \text{ amps.}$$

Faraday's Laws—Example

PROBLEM 231.—A current passed for $t = 6$ minutes through a voltameter containing diluto H_2SO_4 liberated

40 c.c. of electrolytic gas, measured at 15° C. and 748 mm. What was the average value of the current?

SOLUTION 231.—If C is the average value of the current in amperes, then during the time t minutes = 60 t seconds

$W = 60\ Ct = 60 \times 6 \times C$ coulombs pass through the solution. At 0° C. and 760 mm. the volume occupied by 40 c.c. at 15° C. and 748 mm. is

$$v = \frac{748 \times 40}{288} \times \frac{273}{760} = 37{\cdot}33 \text{ c.c.}$$

But 96540 coulombs liberate 1 gram-equivalent of hydrogen and 1 gram-equivalent of oxygen. At 0° C. and 760 mm. 1 gram-equivalent of hydrogen (1 gram) occupies $\frac{22400}{2}$ = 11200 c.c., and 1 gram-equivalent of oxygen (8 grams) occupies $\frac{22400}{4}$ = 5600 c.c. The total volume at 0° C. and 760 mm. occupied by the electrolytic gas liberated by 96540 coulombs, is, therefore, 16800 c.c.

Since the amount of electrolyte decomposed is proportional to the quantity of electricity

$$\frac{60 \times 6 \times C}{96540} = \frac{37{\cdot}33}{16800},$$

$$\therefore C = \frac{37{\cdot}33 \times 96540}{16800 \times 60 \times 6} = 0{\cdot}596 \text{ amp.}$$

Specific and Equivalent Conductivity—Degree of Dissociation

The specific resistance of a conductor is the resistance in ohms of a regular cube of the substance of side 1 cm. long. The reciprocal of this quantity is the specific conductivity κ. The unit of specific conductivity is, therefore, that of a substance of which the specific resistance is 1 ohm; this unit is called the reciprocal ohm or mho, for which, in future, we shall use the contraction r.o. According to Ohm's law, the specific conductivity gives the current in amperes produced in a regular cube of 1 cm. side when a potential difference of 1 volt is applied between two opposite faces of the cube.

If v is the volume in litres containing 1 gram-equivalent of an electrolyte, the concentration of which is, therefore, $c = \frac{1}{v}$ gram-equivalents per litre, and of which the specific conductivity is κ, the equivalent conductivity of the solution is

(4) $\Lambda = \kappa \times 1000\, v = \frac{1000\,\kappa}{c}$ recip. ohms. If Λ_∞ is the equivalent conductivity at infinite dilution, that is, when the dissociation of the electrolyte is complete, the degree of dissociation in the solution of equivalent conductivity Λ is, according to Arrhenius,

$$(5)\quad \alpha = \frac{\Lambda}{\Lambda_\infty}.$$

Velocity of Migration—Ionic Conductivity

If μ_A and μ_C are the velocities of migration of anion and cation respectively in cms. per second under a potential gradient of 1 volt per cm., then the equivalent conductivity

$$(6)\quad \Lambda = \alpha \times 96540\ (\mu_A + \mu_C)$$
$$(7)\quad = \alpha\,(l_A + l_C),$$

where $l_A = 96540\ \mu_A$ and $l_C = 96540\ \mu_C$ are the equivalent ionic conductivities at infinite dilution of anion and cation respectively (Kohlrausch). When $\alpha = 1$, that is, when the dissociation is complete, equation (7) becomes

$$(8)\quad \Lambda_\infty = l_A + l_C,$$

or, in words, the equivalent conductivity at infinite dilution is equal to the sum of the equivalent ionic conductivities.

Molecular Conductivity

The molecular conductivity μ of a solution of an electrolyte is

$$(9)\quad \mu = 1000\,\kappa v = \frac{1000\,\kappa}{c}\ \text{recip. ohms},$$

where v is the volume in litres containing 1 gram-molecule and c the concentration in gram-molecules per litre. The relation between Λ and μ is

$$\mu = a\Lambda \text{ and } \mu_\infty = a\Lambda_\infty,$$

where a is the number of gram-equivalents contained in 1 gram-molecule.

Dilution Law—Dissociation-constant

If α is the degree of dissociation of a binary electrolyte, and c its concentration in gram-equivalents (or gram-molecules)

per litre, the concentration of each of the ions is ac and that of the undissociated electrolyte $(1 - a)c$. For the dissociation of a binary electrolyte the law of mass-action, therefore, assumes the form

$$(10)\quad \frac{(ac)^2}{(1-a)c} = \frac{a^2c}{(1-a)} = \frac{a^2}{(1-a)v} = K.$$

v is the dilution in litres per gram-equivalent (or gram-molecule) and K the dissociation-constant. This is Ostwald's dilution law. It holds only for weak electrolytes, that is, only with such electrolytes does K remain constant with varying concentration.

Since $a = \frac{\Lambda}{\Lambda_\infty}$, equation (10) may be written in the form

$$(11)\quad \frac{\left(\frac{\Lambda}{\Lambda_\infty}\right)^2}{\left(1 - \frac{\Lambda}{\Lambda_\infty}\right)v} = \frac{\Lambda^2}{\Lambda_\infty(\Lambda_\infty - \Lambda)v} = K.$$

From these equations it is evident that the numerical value of K depends on the unit of concentration or dilution chosen. Here we shall work throughout with the units given above.

In the case of very weak electrolytes, where a and K are very small, $(1 - a)$ in equation (10) may, without sensible error, be put equal to 1, since a in such cases is very small, compared with 1. We thus obtain from (10) and (11) the simplified formulæ

$$(12)\quad a^2c = \frac{a^2}{v} = K,$$

and

$$(13)\quad \frac{\Lambda^2 c}{\Lambda^2_\infty} = \frac{\Lambda^2}{\Lambda^2_\infty v} = K.$$

In a great many cases these simplified formulæ can be used with sufficient approximation.

Electrolytic Dissociation—Examples

PROBLEM 232.—The specific conductivity of a $c_1 = 0{\cdot}1$ N-acetic acid solution at 18° is $\kappa_1 = 0{\cdot}000471$ r.o., and that of a $c_2 = 0{\cdot}001$ N-sodium acetate solution is $\kappa_2 = 0{\cdot}0000781$ r.o. What is the dissociation constant K of acetic acid at 18°, if the ionic conductivity of the H'-ion is $l_o = 318$, and that

of the $Na^{\cdot}$-ion is $l'_C = 44{\cdot}4$, and if the sodium acetate solution is regarded as completely dissociated?

SOLUTION 232.—From (4) we obtain Λ, the equivalent conductivity of c_1 N-acetic acid,

$$\Lambda = \frac{1000\,\kappa_1}{c_1} = \frac{1000 \times 0{\cdot}000471}{0{\cdot}1} = 4{\cdot}71 \text{ r.o.}$$

According to (8), Λ_∞, the equivalent conductivity of acetic acid at infinite dilution, is equal to $l_A + l_C$, where l_A is the ionic conductivity of the anion of acetic acid, $C_2H_3O'_2$, and l_C that of the $H^{\cdot}$-ion. l_C is given, and l_A may be calculated from the equivalent conductivity of the c_2 N-sodium acetate solution, which is equal to Λ'_∞, the equivalent conductivity of sodium acetate at infinite dilution, as the salt is regarded as completely dissociated.

For sodium acetate, therefore,

$$\Lambda'_\infty = l_A + l'_C = \frac{1000\,\kappa_2}{c_2},$$

$$\therefore\ l_A = \frac{1000\,\kappa_2}{c_2} - l'_C = \frac{1000 \times 0{\cdot}0000781}{0{\cdot}001} - 44{\cdot}4$$

$$= 78{\cdot}1 - 44{\cdot}4 = 33{\cdot}7 \text{ r.o.}$$

For acetic acid, therefore,

$$\Lambda_\infty = l_A + l_C = 33{\cdot}7 + 318 = 351{\cdot}7,$$

and, from (5),

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{4{\cdot}71}{351{\cdot}7} = 0{\cdot}0134.$$

Since α is known the dissociation-constant of acetic acid may now be calculated; according to Ostwald's dilution law (10)

$$K = \frac{\alpha^2 c_1}{1 - \alpha} = \frac{(0{\cdot}0134)^2 \times 0{\cdot}1}{0{\cdot}987} = 1{\cdot}8 \times 10^{-5}.$$

PROBLEM 233.—The velocity-constant for the inversion of cane sugar by $c = 0{\cdot}25$ N-acetic acid at 25° is $k = 0{\cdot}75 \times 10^{-3}$. If the velocity-constant is assumed to be proportional to the $H^{\cdot}$-ion concentration, find the value of the constant when the acid solution is also $c_1 = 0{\cdot}025$ N with respect to sodium acetate, being given that the dissociation-constant of acetic acid is $K = 0{\cdot}000018$, and that the sodium acetate is dissociated to the extent of $\alpha_1 = 86$ per cent.

SOLUTION 233.—Let a be the degree of dissociation of the pure acetic acid solution, then, according to (10)

$$\frac{a^2c}{(1-a)} = K \text{ or } \frac{0{\cdot}25a^2}{(1-a)} = 0{\cdot}000018$$

$$\therefore a = 0{\cdot}00845.$$

The concentration of hydrogen ions in the solution is, therefore,

$$[H\cdot] = ac = 0{\cdot}00845 \times 0{\cdot}25 = 2{\cdot}11 \times 10^{-3} \text{ N.}$$

Let a_2 be the degree of dissociation of the acetic acid in the solution containing sodium acetate. The degree of dissociation of the latter is a_1. The concentration of H·-ions derived from the dissociation of the acetic acid is, therefore, a_2c, of the $C_2H_3O'_2$-ions a_2c, and of the undissociated acetic acid $(1 - a_2)c$, whilst the concentration of the $C_2H_3O'_2$-ions derived from the sodium acetate is a_1c_1. The total concentration of the $C_2H_3O'_2$-ions is, therefore, $a_2c + a_1c_1$. Hence, if we use square brackets to denote the concentrations of the enclosed substances,

$$\frac{[H\cdot]_1\,[C_2H_3O'_2]}{[C_2H_4O_2]} = \frac{a_2c(a_2c + a_1c_1)}{(1-a_2)c} = K$$

and, substituting the numerical values,

$$\frac{a_2 \times (0{\cdot}25)^2 \times (a_2 \times 0{\cdot}25 + 0{\cdot}86 \times 0{\cdot}025)}{(1-a_2) \times 0{\cdot}25} = 0{\cdot}000018,$$

$$\therefore a_2 = 8{\cdot}32 \times 10^{-4}$$

and $[H\cdot]_1 = a_2c = 8{\cdot}32 \times 10^{-4} \times 0{\cdot}25 = 2{\cdot}08 \times 10^{-4}$.

If k_1 is the velocity-constant for the mixed solution, then since the velocity-constant is proportional to the H·-ion concentration, we obtain

$$\frac{k_1}{k} = \frac{[H\cdot]_1}{[H\cdot]} \text{ and } k_1 = \frac{k[H\cdot]_1}{[H\cdot]} = \frac{0{\cdot}75 \times 10^{-3} \times 2{\cdot}08 \times 10^{-4}}{2{\cdot}11 \times 10^{-3}}$$

$$= 7{\cdot}39 \times 10^{-5}.$$

To illustrate the degree of approximation attained by the use of formula (12) instead of (10), we shall work the problem on the assumption that a may be neglected in comparison with 1.

For the degree of dissociation of acetic acid in the pure aqueous solution we obtain from (12)

$$a^2c = K,$$

$$a = \sqrt{\frac{K}{c}} = \sqrt{\frac{0{\cdot}000018}{0{\cdot}25}} = 8{\cdot}48 \times 10^{-3},$$

and, therefore,

$$[H\cdot] = ac = 8{\cdot}48 \times 10^{-3} \times 0{\cdot}25 = 2{\cdot}12 \times 10^{-3}.$$

In the mixed solution we may assume that the acetic acid, in presence of the excess of $C_2H_3O'_2$-ions from the dissociation of the sodium acetate, is practically undissociated, that is, $[C_2H_4O_2] = c$, and that the $C_2H_3O'_2$-ions are furnished only by the sodium acetate. Therefore $[C_2H_3O'_2] = a_1c_1$ and

$$\frac{[H\cdot]_1\,[C_2H_3O'_2]}{[C_2H_4O_2]} = \frac{[H\cdot]_1 a_1 c_1}{c} = K,$$

$$[H\cdot]_1 = \frac{Kc}{a_1c_1} = \frac{0{\cdot}000018 \times 0{\cdot}25}{0{\cdot}86 \times 0{\cdot}025} = 2{\cdot}09 \times 10^{-4}.$$

Since,

$$\frac{k_1}{k} = \frac{[H\cdot]_1}{[H\cdot]},$$

$$k_1 = \frac{k\,[H\cdot]_1}{[H\cdot]} = \frac{0{\cdot}75 \times 10^{-3} \times 2{\cdot}09 \times 10^{-4}}{2{\cdot}12 \times 10^{-3}} = 7{\cdot}4 \times 10^{-5}.$$

PROBLEM 234.—The angle of rotation of an $a = 5$ per cent. cane sugar solution in a tube 20 cms. long is $A_0 = +66{\cdot}7°$. After complete inversion the angle of rotation is $A_\infty = -19{\cdot}7°$. If the solution contains in addition $c_1 = 0{\cdot}01$ N-HCl, the angle of rotation diminishes by 69·2° in $t = 20$ minutes. By how much does the angle of rotation diminish in the same time, when, instead of HCl, the solution contains $c_2 = 0{\cdot}1$ N-lactic acid, if the dissociation-constant of lactic acid is $K = 1{\cdot}4 \times 10^{-4}$? Assume the HCl to be completely dissociated.

SOLUTION 234.—If A_0 denotes the initial angle of rotation, before the inversion begins, and A_∞ the final angle of rotation after complete inversion, the total change in the angle of rotation, $A_0 - A_\infty$, is proportional to the initial amount of cane sugar, a per cent. Similarly, if at the time t, when the solution contains x per cent. of cane sugar, the angle of rotation is A_x, the change in the angle of rotation, $A_x - A_\infty$, is proportional to x. Therefore,

$$(1)\quad \frac{A_0 - A_\infty}{A_x - A_\infty} = \frac{a}{x}.$$

Since in the presence of a large excess of water the inversion proceeds as a monomolecular reaction, the velocity of inversion is given by the equation

$$\frac{dx}{dt} = - kx,$$

where k is the velocity-constant of the reaction, and x the concentration of the cane sugar at the time t. On integrating we obtain

$$(2)\ \log_e x = - kt + \text{constant.}$$

When $t = 0$, $x = a$,

$$(3)\ \therefore \log_e a = \text{constant.}$$

Subtracting (2) from (3) we obtain

$$\log_e \frac{a}{x} = kt,$$

and, therefore, from (1)

$$kt = \log_e \frac{A_o - A_\infty}{A_x - A_\infty},$$

or, changing from natural to common logarithms,

$$(4)\ k = \frac{2{\cdot}3}{t} \log \frac{A_o - A_\infty}{A_x - A_\infty}.$$

The inversion is catalytically accelerated by the H·-ions, and the velocity-constant k is proportional to the H·-ion concentration. If we assume the HCl to be completely dissociated, the concentration of the H·-ions is $[H\cdot]_1 = c_1$. The velocity-constant k_1 for this particular case may be calculated from the data given in the problem by means of equation (4) which in this case becomes

$$(5)\ k_1 = \frac{2{\cdot}3}{t} \log \frac{A_o - A_\infty}{A_x - A_\infty}.$$

In the c_2. N-lactic acid let the H·-ion concentration be $[H\cdot]_2$. If, for brevity, we represent lactic acid by the formula LH, where L is the anion, we obtain for the dissociation of lactic acid the equilibrium-equation

$$\frac{[L'][H\cdot]_2}{[LH]} = K,$$

or, since $[L'] = [H\cdot]_2$,

$$\frac{[H\cdot]_2^2}{(c_2 - [H\cdot]_2)} = K,$$

$$[H\cdot]_2^2 = K(c_2 - [H\cdot]_2),$$

$$\text{and } [H\cdot]_2 = -\frac{K}{2} + \sqrt{\frac{K^2}{4} + Kc_2}.$$

If k_2 is the velocity-constant for the inversion of cane sugar by c_2 N-lactic acid, we obtain, since the velocity-constant is proportional to the H·-ion concentration,

$$(6)\quad \frac{k_1}{k_2} = \frac{[H\cdot]_1}{[H\cdot]_2} = \frac{c_1}{\sqrt{\frac{K^2}{4} + Kc_2} - \frac{K}{2}}.$$

In this equation only k_2 is unknown, and can, therefore, be calculated.

The angle of rotation A_y in the lactic acid solution after t minutes is obtained from the equation (cf. (4))

$$(7)\quad \log\frac{A_o - A_\infty}{A_y - A_\infty} = \frac{k_2 t}{2\cdot 3}.$$

Substituting the numerical values in the various equations we obtain k_1, k_2 and A_y, and, therefore, the diminution of the angle of rotation required, $A_o - A_y$. Thus in the case of the inversion by HCl, since the diminution of the angle of rotation after 20 minutes is 69·2°, we obtain $A_x = 66{\cdot}7° - 69{\cdot}2° = -2{\cdot}5°$, and from equation (5)

$$k_1 = \frac{2\cdot 3}{t}\log\frac{A_o - A_\infty}{A_x - A_\infty}$$

$$= \frac{2\cdot 3}{20}\log\frac{66{\cdot}7 + 19{\cdot}7}{-2{\cdot}5 + 19{\cdot}7} = 0{\cdot}115\log\frac{86{\cdot}4}{17{\cdot}2}$$

$$= 0{\cdot}115 \times 0{\cdot}703 = 0{\cdot}0808.$$

From (6)

$$k_2 = \frac{k_1}{c_1}\left(\sqrt{\frac{K^2}{4} + Kc_2} - \frac{K}{2}\right)$$

$$= \frac{0{\cdot}0808}{0{\cdot}01}\left(\sqrt{\frac{(1{\cdot}4)^2 \times 10^{-8}}{4} + 1{\cdot}4 \times 10^{-4} \times 0{\cdot}1} - \frac{1{\cdot}4 \times 10^{-4}}{2}\right)$$

$$= 8{\cdot}08\,(\sqrt{0{\cdot}49 \times 10^{-8} + 1{\cdot}4 \times 10^{-5}} - 0{\cdot}7 \times 10^{-4})$$
$$= 8{\cdot}08\,(3{\cdot}74 \times 10^{-3} - 0{\cdot}7 \times 10^{-4})$$
$$= 0{\cdot}0297.$$

From (7)

$$\log(A_y - A_\infty) = \log(A_o - A_\infty) - \frac{k_2 t}{2{\cdot}3}$$
$$= \log 86{\cdot}4 - \frac{0{\cdot}0297 \times 20}{2{\cdot}3}$$
$$= 1{\cdot}937 - 0{\cdot}258 = 1{\cdot}679,$$
$$\therefore A_y - A_\infty = 47{\cdot}8°,$$
$$\text{and } A_y = 47{\cdot}8 + A_\infty = 47{\cdot}8 - 19{\cdot}7 = 28{\cdot}1°.$$

The diminution of the angle of rotation after 20 minutes in the lactic acid solution is, therefore,

$$A_o - A_y = 66{\cdot}7° - 28{\cdot}1° = 38{\cdot}6°.$$

PROBLEM 235 (cf. preceding problem).—What is the dissociation-constant of acetic acid if a mixture of $c_3 = 0{\cdot}05$ N-lactic acid, and $c_4 = 0{\cdot}38$ N-acetic acid has the same inverting action as the $c_2 = 0{\cdot}1$ N-lactic acid alone?

SOLUTION 235.—If a solution containing c_3 N-lactic acid and c_4 N-acetic acid has the same inverting action as a c_2 N-lactic acid solution alone, the H·-ion concentrations of these two solutions must be the same, since the inverting action is proportional to the H·-ion concentration.

If, for brevity, we represent lactic and acetic acids by the formulæ LH and AH, where L and A are the respective anions, we obtain for the electrolytic dissociation of lactic acid

$$(1)\quad \frac{[\mathrm{L'}]\,[\mathrm{H\cdot}]}{[\mathrm{LH}]} = K,$$

and of acetic acid

$$(2)\quad \frac{[\mathrm{A'}]\,[\mathrm{H\cdot}]}{[\mathrm{AH}]} = K',$$

where K and K' are the dissociation-constants of lactic acid and acetic acid respectively. As in Solution 234 we have also

$$(3)\quad [\mathrm{H\cdot}] = \sqrt{\frac{K^2}{4} + Kc_2} - \frac{K}{2},$$

and in the mixed solution

$$(4)\ [L'] + [LH] = c_3,$$
$$(5)\ [A'] + [AH] = c_4,$$

and

$$(6)\ [L'] + [A'] = [H\cdot].$$

From these six equations the six unknown quantities

$[L']$, $[A']$, $[LH]$, $[AH]$, $[H\cdot]$ and K' may be calculated.

From (3)

$$[H\cdot] = \sqrt{\frac{(1\cdot4)^2 \times 10^{-8}}{4} + 1\cdot4 \times 10^{-5}} - \frac{1\cdot4 \times 10^{-4}}{2}$$
$$= 3\cdot67 \times 10^{-3},$$

and from (4)

$$[L'] = c_3 - [LH] = 0\cdot05 - [LH].$$

Substituting these values of $[H\cdot]$ and $[L']$ and the numerical value of K in (1) we obtain

$$(0\cdot05 - [LH]) \times 3\cdot67 \times 10^{-3} = 1\cdot4 \times 10^{-4}\,[LH],$$
$$\therefore [LH] = \frac{1\cdot835 \times 10^{-4}}{3\cdot81 \times 10^{-3}} = 0\cdot04818,$$

and, therefore, from (4)

$$[L'] = 0\cdot05 - 0\cdot04818 = 0\cdot00182.$$

From (6)

$$[A'] = [H\cdot] - [L'] = 0\cdot00367 - 0\cdot00182 = 0\cdot00185.$$

From (5)

$$[AH] = c_4 - [A'] = 0\cdot38 - 0\cdot00185 = 0\cdot378,$$

and, finally, from (2)

$$K' = \frac{[A'][H\cdot]}{[AH]}$$
$$= \frac{0\cdot00185 \times 0\cdot00367}{0\cdot378}$$
$$= 1\cdot8 \times 10^{-5}.$$

PROBLEM 236.—In a mineral water with an acid reaction the total concentration of carbonic acid, free and combined, is $a = 0\cdot620$ gram CO_2 per litre, the total concentration of sulphuretted hydrogen, free and combined, is $b = 0\cdot018$ gram H_2S per litre, and the concentration of sodium oxide is $c =$

0·279 gram Na_2O per litre. What is the concentration of free carbonic acid $[H_2CO_3]$ and of free sulphuretted hydrogen $[H_2S]$, if the first dissociation-constant of H_2CO_3 is $K_1 = 3{\cdot}04 \times 10^{-7}$, and that of H_2S is $0{\cdot}91 \times 10^{-7}$?

SOLUTION 236.—In the acid mineral water the carbon dioxide is present as undissociated molecules of carbonic acid H_2CO_3 and as the anion HCO'_3, and the hydrogen sulphide is present as undissociated H_2S and as the anion HS'.

If M_1 is the molecular weight of CO_2 and M_2 that of H_2S then

$$(1)\ [H_2CO_3] + [HCO'_3] = \frac{a}{M_1},$$

$$(2)\ [H_2S] + [HS'] = \frac{b}{M_2},$$

where the square brackets denote, as usual, the concentrations of the enclosed substances.

From the law of electro-neutrality, according to which the total number of equivalents of cations must be equal to the total number of equivalents of anions in the solution, it follows that

$$(3)\ [HCO'_3] + [HS'] = [Na\cdot] = \frac{2c}{M_3},$$

where M_3 denotes the molecular weight of Na_2O. For the solution of these three equations with the four unknowns $[H_2CO_3]$, $[H_2S]$, $[HCO'_3]$ and $[HS']$, a fourth equation is required. This is obtained by an application of the law of mass-action.

For the ionic dissociation of the two weak acids the following equations hold,

$$[HCO'_3]\ [H\cdot] = K_1\ [H_2CO_3]$$

and

$$[HS']\ [H\cdot] = K_2\ [H_2S],$$

or, dividing the latter by the former,

$$(4)\ \frac{[HS']}{[HCO'_3]} = \frac{K_2}{K_1}\frac{[H_2S]}{[H_2CO_3]}.$$

The problem is, therefore, capable of solution.

From a consideration of the numerical values given in the problem, it follows that $[HS']$ is small compared with $[HCO'_3]$, especially as hydrogen sulphide is the weaker acid. Neglect-

ing [HS′] in comparison with [HCO_3'], we therefore obtain from (3)

$$[HCO_3'] = \frac{2c}{M_3} = \frac{2 \times 0{\cdot}279}{62} = 0{\cdot}009 \text{ gm.-ion per litre,}$$

and from (1)

$$[H_2CO_3] = \frac{a}{M_1} - 0{\cdot}009 = 0{\cdot}0141 - 0{\cdot}009 = \mathbf{0{\cdot}0051} \text{ mole per litre.}$$

From (4) we thus obtain

$$(5)\quad \frac{[HS']}{[H_2S]} = \frac{0{\cdot}91 \times 10^{-7}}{3{\cdot}04 \times 10^{-7}} \times \frac{0{\cdot}009}{0{\cdot}0051} = 0{\cdot}53,$$

and $[HS'] = 0{\cdot}53\,[H_2S]$. Substituting this value of [HS′] in equation (2) we have

$$[H_2S]\,(1 + 0{\cdot}53) = \frac{b}{M_2} = 0{\cdot}00053,$$

$$\therefore\ [H_2S] = \mathbf{0{\cdot}000346} \text{ gram-molecule per litre,}$$

and

$$[HS'] = 0{\cdot}000184 \text{ gram-ion per litre.}$$

PROBLEM 237.—When picric acid distributes itself between water and benzene, only the undissociated molecules of the acid dissolve in the benzene, and the partition-coefficient of the undissociated molecules for benzene/water is $K_1 = 1/0{\cdot}0281$. The dissociation-constant of picric acid in water is $K_2 = 0{\cdot}164$. What is the concentration c_0 of an aqueous solution of picric acid which is in equilibrium with a $c = 0{\cdot}07$ N-solution of picric acid in benzene?

SOLUTION 237.—Picric acid is soluble both in water and in benzene; if an aqueous solution of picric acid is shaken with benzene, the picric acid distributes itself between the two solvents and the ratio of the concentrations of the undissociated picric acid molecules in the two solvents has a constant value K_1, which is independent of the concentration. The aqueous solution conducts the electric current, and, therefore, contains the ions of picric acid besides undissociated molecules; the benzene solution, on the other hand, contains no ions since it is a non-conductor.

Let the total concentration of an aqueous solution, which is in equilibrium with a c N-benzene solution, be $c_0 = c_1 + c_2$, where c_1 is the concentration of the undissociated molecules

and c_2 that of the ions. At equilibrium the following equations must hold:—

(1) from the partition law, $\frac{c}{c_1} = K_1$,

(2) from Ostwald's dilution law $\frac{c_2^2}{c_1} = K_2$.

From these two equations and the further equation $c_0 = c_1 + c_2$, the three unknowns c_0, c_1 and c_2 may be calculated.

By dividing (1) by (2) we obtain

$$c = c_2^2 \frac{K_1}{K_2} \text{ and } c_2 = \sqrt{\frac{cK_2}{K_1}};$$

from (1)

$$c_1 = \frac{c}{K_1};$$

therefore

$$\begin{aligned} c_0 &= c_1 + c_2 \\ &= \frac{c}{K_1} + \sqrt{\frac{cK_2}{K_1}} \\ &= 0{\cdot}07 \times 0{\cdot}0281 + \sqrt{0{\cdot}07 \times 0{\cdot}0281 \times 0{\cdot}164} \\ &= \mathbf{0{\cdot}0200} \text{ N.} \end{aligned}$$

PROBLEM 238.—A methyl acetate solution is saponified by a $c_1 = 0{\cdot}1$ N-solution of KCN $a = 3{\cdot}3$ times as fast as by a $c_2 = 0{\cdot}01$ N-solution. What is the dissociation-constant K of hydrocyanic acid, if the ionic product of water is $K_w = 0{\cdot}8 \times 10^{-14}$?

SOLUTION 238.—The solution of KCN is alkaline on account of hydrolysis, and in alkaline solution the saponification of the ester takes place according to the equation

$$CH_3COOCH_3 + OH' = CH_3OH + CH_3COO'.$$

The velocity of saponification is, therefore, proportional to the product of the concentrations of the ester and of the free hydroxyl ions. In two solutions, in which the concentrations of the ester are equal, the velocities of saponification are, therefore, proportional to the concentrations of the hydroxyl ions $[OH']_1$ and $[OH']_2$. In the present case we have, therefore,

$$(1)\ \frac{[OH']_1}{[OH']_2} = a.$$

From the law of mass-action we obtain for the dissociation of hydrocyanic acid

$$\frac{[CN'][H\cdot]}{[HCN]} = K,$$

and, since $[H\cdot][OH'] = K_w$,

$$(2)\ \frac{[CN']}{[HCN]} = \frac{K}{K_w}[OH'].$$

The concentration of the undissociated KCN may be neglected, since the salt may be regarded as completely dissociated. The concentration of the K·-ions is, therefore, practically equal to the total concentration c of the KCN. The principle of electro-neutrality requires

$$c = [K\cdot] = [CN'] + [OH'],$$

as the hydrolysis of KCN takes place according to the equation

$$KCN + H_2O = HCN + KOH,$$

and the KOH like the KCN may be regarded as completely dissociated.

We obtain, therefore,

$$(3)\ c_1 = [CN']_1 + [OH']_1,$$

$$\text{and } (4)\ c_2 = [CN']_2 + [OH']_2 = [CN']_2 + \frac{[OH']_1}{a} \text{ (from (1))}.$$

For the solution of the three equations (2), (3) and (4), in which the five quantities K, $[HCN]$, $[CN']_1$, $[CN']_2$ and $[OH']_1$ are unknown, we require two further equations. These we obtain as follows. The concentration of the OH'-ions produced by the hydrolysis is equal to the concentration of the undissociated HCN produced at the same time according to the equation

$$CN' + H_2O = OH' + HCN.$$

Therefore, from (2),

$$[HCN] = [OH'] = \frac{[CN']}{[OH']} \times \frac{K_w}{K},$$

and

$$(5)\ [CN']_1 = \frac{K[OH']_1^2}{K_w}$$

and

$$(6)\ [CN']_2 = \frac{K[OH']_2^2}{K_w} = \frac{K}{K_w} \times \frac{[OH']_1^2}{a^2}$$

By dividing (5) by (6) we obtain

$$\frac{[CN']_1}{[CN']_2} = a^2,$$

and, from (4),

$$(7)\ c_2 = \frac{[CN']_1}{a^2} + \frac{[OH']_1}{a}.$$

From (3) and (7) we obtain

$$\frac{[CN']_1}{a} - \frac{[CN']_1}{a^2} = \frac{c_1}{a} - c_2,$$

$$\therefore [CN']_1 = \frac{a(c_1 - c_2 a)}{a - 1}$$

and

$$[OH']_1 = c_1 - [CN']_1 = \frac{a^2 c_2 - c_1}{a - 1}.$$

Finally, from (5),

$$\begin{aligned} K &= \frac{K_w [CN']_1}{[OH']_1^2}, \\ &= K_w \frac{a(c_1 - c_2 a)(a - 1)}{(a^2 c_2 - c_1)^2} \\ &= \frac{0{\cdot}8 \times 10^{-14} \times 3{\cdot}3 \times 2{\cdot}3 \times (0{\cdot}1 - 0{\cdot}033)}{\{(3{\cdot}3)^2 \times 0{\cdot}01 - 0{\cdot}1\}^2} \\ &= \mathbf{5 \times 10^{-11}}. \end{aligned}$$

Transport Numbers

If μ_A and μ_C are the velocities of migration of the anion and cation respectively, the fraction $\frac{\mu_A}{\mu_A + \mu_C} = n$ is called the transport number (migration number) of the anion, and the fraction $\frac{\mu_C}{\mu_A + \mu_C} = 1 - n$ the transport number of the cation (Hittorf). Of the total quantity of electricity which passes any cross-section of an electrolyte, the fraction n is carried

by the anions or negative ions and the fraction $1 - n$ by the cations or positive ions. From equations (6), (7) and (8) it is evident that

$$n = \frac{l_A}{l_A + l_C} = \frac{l_A}{\Lambda_\infty} \text{ and } 1 - n = \frac{l_C}{l_A + l_C} = \frac{l_C}{\Lambda_\infty},$$

so that from a knowledge of n and Λ_∞ we can obtain l_A and l_C.

n is determined experimentally by electrolysing a solution of the electrolyte in question, measuring the total quantity of electricity which has passed through the solution (e.g. by a silver voltameter in series with the electrolyte) and the changes of concentration at the electrodes. If the quantity of electricity F is passed through the solution, 1 gram-equivalent of anion is deposited at the anode, n gram-equivalent of anion migrates to the anode, and $1 - n$ gram-equivalent of cation migrates from the anode, that is, at the anode $1 - n$ gram-equivalent of both anion and cation disappears, or $1 - n$ gram-equivalent is the fall in concentration of the electrolyte round the anode. Similarly at the cathode, 1 gram-equivalent of cation is deposited, $1 - n$ gram-equivalent of cation migrates to the electrode, and n gram-equivalent of anion migrates from the electrode, that is, at the cathode n gram-equivalent of both cation and anion disappears from the solution round the electrode, or the fall in concentration of the solution round the cathode is n gram-equivalent. If then we assume that the changes in concentration round the electrodes are due only to discharge and migration of the ions, that no secondary changes, such as solution of the electrodes, etc., take place, and that no diffusion occurs, we have the relation

$$\frac{\text{fall of conc. of electrolyte round cathode}}{\text{fall of conc. of electrolyte round anode}} = \frac{n}{1 - n}.$$

Since the quantities on the left-hand side of the equation are known, n may be calculated.

It is not, however, necessary to determine the change in concentration at both electrodes. If the theoretical change (fall) in concentration in gram-equivalents at one electrode, say the cathode, and the total quantity of electricity in coulombs passed through the solution (e.g. by the silver voltameter) are determined, all the necessary data are obtained. Then

$$\frac{\text{fall (in gram-equivs.) round cathode} \times 96540}{\text{total quantity of electricity passed}} = n,$$

or

$$\frac{\text{fall (in gram-equivs.) round anode} \times 96540}{\text{total quantity of electricity passed}} = 1 - n.$$

Since, however, the experimental arrangements for the determination of transport numbers vary with the nature of the ions under investigation, and secondary reactions at the electrodes, which vary from case to case, have to be taken into account, the calculation for each particular case has to be thought out independently.

Transport Numbers—Example

PROBLEM 239. — A solution containing 0·1605 per cent. NaOH was electrolysed between platinum electrodes. After electrolysis 55·25 grams of the cathode solution contained 0·09473 grams NaOH, whilst the concentration of the middle portion of the electrolyte was unchanged. In a silver voltameter in series the equivalent of 0·0290 gram NaOH was deposited during electrolysis. Calculate the transport numbers of the $Na^{\cdot}$ and OH' ions.

SOLUTION 239. — After electrolysis 55·25 grams of the cathode solution contained 0·09473 gram NaOH or (55·25 − 0·09473 =) 55·155 grams of water contained 0·09473 gram NaOH.

Before electrolysis 100 grams of the cathode solution contained 0·1605 gram NaOH, therefore, 55·155 grams water contained $\frac{0{\cdot}1605 \times 55{\cdot}155}{100 - 0{\cdot}1605} = 0{\cdot}08867$ gram NaOH.

The increase in the amount of NaOH round the cathode is therefore, 0·09473 − 0·08867 = 0·00606 gram.

At the cathode, however, the secondary reaction

$$Na + H_2O = NaOH + H$$

takes place, the discharged $Na^{\cdot}$-ions reacting with the water to re-form their equivalent of NaOH. Had no secondary reaction taken place, therefore, the cathode solution would have contained 0·0290 gram NaOH less than it did, since 0·0290 gram NaOH is the equivalent of the $Na^{\cdot}$-ions discharged, as measured by the silver voltameter. The amount of NaOH in the cathode solution would, therefore, have been

0·09473 − 0·0290 = 0·06573 gram in 55·155 grams water, compared with 0·08867 gram before electrolysis. The theoretical fall in concentration round the cathode, that is, on the assumption that no secondary reaction had taken place, is, therefore, 0·08867 − 0·06573 = 0·02294 gram NaOH. If M is the equivalent weight of NaOH we obtain

$$\mathbf{n} = \frac{\text{fall in gram-equivs. round cathode} \times 96540}{\text{total quantity of electricity passed}}$$

$$= \frac{\frac{0{\cdot}02294}{M} \times 96540}{\frac{0{\cdot}0290}{M} \times 96540} = \frac{0{\cdot}02294}{0{\cdot}0290} = \mathbf{0{\cdot}791}$$

and $\mathbf{1 - n = 1 - 0{\cdot}791 = 0{\cdot}209.}$

Alternative Method.—For the deposition of $\frac{0{\cdot}0290}{M}$ gram-equivalent of silver in the voltameter, the increase in the amount of NaOH round the cathode is $\frac{0{\cdot}00606}{M}$ gram-equiv.

Therefore, for the passage of 1 faraday (96540 coulombs), corresponding to the deposition of 1 gram-equivalent of silver in the voltameter, the increase in the amount of NaOH round the cathode would have been

$$\frac{0{\cdot}00606}{M} \times \frac{1}{0{\cdot}0290/M} = \frac{0{\cdot}00606}{M} \times \frac{M}{0{\cdot}0290} = \frac{0{\cdot}00606}{0{\cdot}0290} \text{ gram-equiv.}$$

But for the passage of 1 faraday n gram-equivalent of OH' migrates from the cathode, $1 - n$ gram-equivalent of $Na\cdot$ migrates to the cathode and 1 gram-equivalent of $Na\cdot$ is discharged at the cathode. The theoretical fall in the amount of electrolyte round the cathode for the passage of 1 faraday is, therefore, n gram-equivalent of OH' and $1 - (1 - n) = n$ gram-equivalent of $Na\cdot$, or n gram-equivalent of NaOH. But owing to the secondary reaction of the discharged gram-equivalent of $Na\cdot$ with the water, 1 gram-equivalent of NaOH is re-formed. Instead of a fall of n gram-equivalent there is, therefore, an increase round the cathode of $1 - n$ gram-equivalent of NaOH. Therefore

$$\mathbf{1 - n} = \frac{0{\cdot}00606}{0{\cdot}0290} = \mathbf{0{\cdot}209,}$$

and $\mathbf{n = 1 - 0{\cdot}209 = 0{\cdot}791.}$

Solubility and Solubility-product

From the law of mass-action it follows that for a saturated solution of a difficultly soluble electrolyte $A_m B_n$ in contact with the solid phase

$$(14)\quad [A^{\cdot}]^m [B']^n = k [A_m B_n] = L,$$

where the square brackets denote the concentration of the enclosed ions or molecules, the former in gram-ions per litre, and the latter in gram-molecules per litre. Since the solution is in equilibrium with solid phase the concentration of the undissociated part $[A_m B_n]$ for a given temperature is constant and independent of any excess of either of the ions $A^{\cdot}$ or B' in the form of another electrolyte with a common ion. The product

$$[A^{\cdot}]^m [B']^n = L$$

is called the solubility-product (or ionic-product) of the electrolyte. For binary electrolytes (14) takes the form

$$(15)\quad [A^{\cdot}] [B'] = L,$$

and since in pure aqueous solution $[A^{\cdot}] = [B']$ we obtain for that case

$$[A^{\cdot}] = [B'] = \sqrt{L}.$$

Further, if the binary electrolyte is very insoluble, and belongs to the class of strong electrolytes, like AgCl, for example, we may regard it as practically completely dissociated in solution, and the concentration of the undissociated part as negligible compared with that of the ions. In such a case

$$(16)\quad \sqrt{L} = S,$$

where S is the solubility of the electrolyte in gram-molecules per litre.

For a ternary electrolyte, e.g. A_2B, we obtain similarly

$$(17)\quad [A^{\cdot}]^2 [B''] = L,$$

and since in pure aqueous solution two ions of A are formed for one of B, the concentration of B'' in gram-ions per litre is half that of $A^{\cdot}$, i.e. $[B''] = [A^{\cdot}]/2$ or $[A^{\cdot}] = 2 [B'']$. Therefore, from (17),

$$(18)\ \frac{[A\cdot]^2\,[A\cdot]}{2} = \frac{[A\cdot]^3}{2} = L$$

or

$$(19)\ 4[B'']^2\,[B''] = 4[B'']^3 = L.$$

Finally, if the ternary electrolyte is a very insoluble, strong electrolyte, so that practically complete dissociation may be assumed, from (18) or (19) the solubility S of the electrolyte in gram-molecules per litre is

$$(20)\ S = [B''] = \frac{[A\cdot]}{2} = \sqrt[3]{\frac{L}{4}},$$

since one molecule of the undissociated electrolyte contains one atom of B and 2 atoms of A.

Solubility-product—Examples

PROBLEM 240.—At 20° the specific conductivity of a saturated solution of silver bromide was $1{\cdot}576 \times 10^{-6}$ r.o. and that of the water used was $1{\cdot}519 \times 10^{-6}$ r.o. On the assumption that the AgBr is completely dissociated, calculate the solubility and solubility-product of AgBr, given that the equivalent conductivities of KBr, KNO_3 and $AgNO_3$ at infinite dilution are 137·4, 131·3 and 121·0 r.o. respectively.

SOLUTION 240. — The specific conductivity κ due to the AgBr alone is (total specific conductivity – specific conductivity of the water used),

$$\therefore\ \kappa = 1{\cdot}576 \times 10^{-6} - 1{\cdot}519 \times 10^{-6} = 0{\cdot}057 \times 10^{-6}\ \text{r.o.}$$

Since the AgBr is assumed to be completely dissociated the equivalent conductivity calculated from the specific conductivity according to (4) is equal to the equivalent conductivity at infinite dilution Λ_∞. Λ_∞ for AgBr may be obtained from (8) as follows :—

$$\begin{aligned}\Lambda_\infty &= l_{Ag\cdot} + l_{Br'} = (l_{Ag\cdot} + l_{NO_3'}) + (l_{K\cdot} + l_{Br'}) - (l_{K\cdot} + l_{NO_3'}\\ &= 121{\cdot}0 + 137{\cdot}4 - 131{\cdot}3\\ &= 127{\cdot}1\ \text{r.o.}\end{aligned}$$

Therefore, from (4),

$$\Lambda_\infty = \frac{1000\kappa}{c},$$

$$127{\cdot}1 = \frac{1000 \times 0{\cdot}057 \times 10^{-6}}{c},$$

$$\therefore c = \frac{1000 \times 0{\cdot}057 \times 10^{-6}}{127{\cdot}1} = 4{\cdot}49 \times 10^{-7}$$

where c is the concentration of the saturated solution, or solubility, in gram-equivalents per litre.

Since the AgBr is completely dissociated, the concentration of both the $Ag^{\cdot}$- and Br'-ions is $4{\cdot}49 \times 10^{-7}$ gram-ion per litre and the solubility-product is

$$L = [Ag^{\cdot}][Br'] = (4{\cdot}49 \times 10^{-7})^2 = 2{\cdot}03 \times 10^{-13}.$$

PROBLEM 241.—At a given temperature a litre of a saturated solution of silver bromate contains $S = 0{\cdot}0081$ gram-molecule of salt; $c = 0{\cdot}0085$ gram-molecule of silver nitrate is then added. Calculate the new solubility S' of silver bromate, assuming that both salts are practically completely dissociated in the solution.

SOLUTION 241.—In the saturated pure aqueous solution the concentration of both the $Ag^{\cdot}$- and BrO_3'-ions is S gram-ion per litre, since the salt is completely dissociated. The solubility-product of $AgBrO_3$ is, therefore,

$$L = [Ag^{\cdot}][BrO_3'] = (S)^2 = (0{\cdot}0081)^2.$$

In any solution saturated with $AgBrO_3$ the product of the concentrations of the $Ag^{\cdot}$- and BrO_3'-ions must be L. Let S' be the solubility, in gram-molecules per litre, of $AgBrO_3$ in the solution containing c N-$AgNO_3$. Since both salts are assumed to be completely dissociated, the concentration of the BrO_3'-ions, derived from the dissociation of the $AgBrO_3$, is S', the concentration of the $Ag^{\cdot}$-ions from the $AgBrO_3$ is also S', and the concentration of the $Ag^{\cdot}$-ions from the $AgNO_3$ is c gram-ions per litre. The total concentration of the $Ag^{\cdot}$-ions is, therefore, $(c + S')$ gram-ions per litre. Therefore

$$L = [Ag^{\cdot}][BrO_3'] = (c + S')(S'),$$

or, putting in the numerical values,

$$(0{\cdot}0085 + S')(S') = (0{\cdot}0081)^2$$

$$\therefore S' = \mathbf{0{\cdot}0049} \text{ gram-molecule per litre.}$$

PROBLEM 242.—The solubility of $Ag_2C_2O_4$ at 25° is $S = 1{\cdot}48 \times 10^{-4}$ gram-molecule per litre. A solution of potassium oxalate, containing $c = 0{\cdot}2942$ gram-molecule per litre, was shaken at 25° with excess of Ag_2CrO_4 till equilibrium was established according to the equation

$$Ag_2CrO_4 + K_2C_2O_4 = Ag_2C_2O_4 + K_2CrO_4.$$

The solution then contained $c_1 = 0{\cdot}0602$ gram-molecule K_2CrO_4 per litre. Assuming that the degrees of dissociation of the oxalate and chromate in the solution are equal and that the dissociation of the silver salts is practically complete, calculate the solubility-product L_{ox} and the solubility S' of Ag_2CrO_4.

SOLUTION 242.—The solubility-product of $Ag_2C_2O_4$ is

$$L_{ox} = [Ag\cdot]^2[C_2O_4''] = (2S)^2(S) = 4S^3$$

since, on complete dissociation, S gram-molecule of $Ag_2C_2O_4$ gives $2S$ gram-ion of $Ag\cdot$ and S gram-ion of C_2O_4'',

$$\therefore\ L_{ox} = 4(1{\cdot}48 \times 10^{-4})^3 = 1{\cdot}3 \times 10^{-11}.$$

In the mixed solution at equilibrium both $Ag_2C_2O_4$ and Ag_2CrO_4 are present as solid phases, therefore the equations

$$(1)\ L_{cr} = [Ag\cdot]^2[CrO_4'']$$

and

$$(2)\ L_{ox} = [Ag\cdot]^2[C_2O_4'']$$

must be simultaneously satisfied. Since the $Ag\cdot$-ion concentration is the same in both, namely that in the solution in equilibrium with the solid phases, we obtain, by dividing (1) by (2),

$$(3)\ \frac{[CrO_4'']}{[C_2O_4'']} = \frac{L_{cr}}{L_{ox}}.$$

The concentration of the K_2CrO_4 at equilibrium is c_1 and of the $K_2C_2O_4$ $(c - c_1)$ gram-molecules per litre. If α is the degree of dissociation of both these salts, the concentrations of the CrO_4''- and C_2O_4''-ions are αc_1 and $\alpha(c - c_1)$ gram-ions per litre respectively.

From (3), therefore,

$$\frac{[CrO_4'']}{[C_2O_4'']} = \frac{\alpha c_1}{\alpha(c - c_1)} = \frac{c_1}{(c - c_1)} = \frac{L_{cr}}{L_{ox}}$$

and

$$L_{cr} = \frac{c_1 \times L_{ox}}{c - c_1}$$

$$= \frac{0{\cdot}0602 \times 1{\cdot}3 \times 10^{-11}}{0{\cdot}2942 - 0{\cdot}0602} = 3{\cdot}34 \times 10^{-12}.$$

If S' gram-molecule per litre is the solubility of Ag_2CrO_4 in pure aqueous solution, and if the salt is completely dissoci-

ated, the concentration of the $Ag^{\cdot}$-ions is $2S'$ and of the CrO_4''-ions S' gram-ions per litre. Therefore

$$[Ag^{\cdot}]^2\,[CrO_4'']=(2S')^2\,(S')=4(S')^3=L_{Cr}$$

and

$$S'=\sqrt[3]{\frac{L_{Cr}}{4}}=\sqrt[3]{\frac{3{\cdot}34\times10^{-12}}{4}}=0{\cdot}94\times10^{-4}\text{ gram-molecule per litre.}$$

PROBLEM 243.—The dissociation-constant of ammonium hydroxide is $K=1{\cdot}8\times10^{-5}$, and the solubility-product of magnesium hydroxide is $L=1{\cdot}22\times10^{-11}$. How many grams of solid ammonium chloride must be added to a mixture of 50 c.c. of N-NH_4OH solution and 50 c.c. of N-$MgCl_2$ solution, so that the precipitate of magnesium hydroxide may just disappear? Assume that the volume of the solution is not changed by dissolving the solid NH_4Cl, and that the dissociation of the neutral salts is complete.

SOLUTION 243.—In any solution saturated with $Mg(OH)_2$ the equation

$$[Mg^{\cdot\cdot}]\,[OH']^2=L$$

must be satisfied. The precipitate of $Mg(OH)_2$ disappears, therefore, in a solution in which the concentration of the OH'-ions is given by the equation

$$[OH']=\sqrt{\frac{L}{[Mg^{\cdot\cdot}]}},$$

where $[Mg^{\cdot\cdot}]$ is equal to the total amount of magnesium present. The equilibrium equation for the electrolytic dissociation of the ammonia in the solution, namely,

$$[NH_4^{\cdot}]\,[OH']=K\,[NH_4OH],$$

must also be satisfied.

The $NH_4^{\cdot}$-ions are derived practically entirely from the solution of the solid ammonium chloride, since the NH_4OH can be regarded as practically undissociated in presence of the NH_4Cl. The concentration of the $NH_4^{\cdot}$-ions, is, therefore,

$$[NH_4^{\cdot}]=\frac{K[NH_4OH]}{[OH']}=K[NH_4OH]\sqrt{\frac{[Mg^{\cdot\cdot}]}{L}}.$$

In order to produce this concentration of NH_4·-ions we must dissolve in the 100 c.c. of solution (= 1/10 litre)

$$x = K[NH_4OH]\sqrt{\frac{[Mg\cdot\cdot]}{L}} \times \frac{M}{10} \text{ grams of } NH_4Cl,$$

where M denotes the molecular weight of NH_4Cl.

Substituting the numerical values in this equation we obtain

$$x = 1{\cdot}8 \times 10^{-5} \times 0{\cdot}5 \times \sqrt{\frac{0{\cdot}5}{1{\cdot}22 \times 10^{-11}}} \times 5{\cdot}35$$

$$= 9{\cdot}8 \text{ grams } NH_4Cl,$$

since the total concentration of both NH_4OH and Mg in the mixed solutions is 0·5 N.

PROBLEM 244.—The solubility of calcium carbonate in pure water is $S = 1{\cdot}3 \times 10^{-4}$ gram-molecules per litre. What is its solubility in water which is saturated with carbon dioxide under a pressure (1) of $p_1 = \frac{1}{20}$ atmosphere, and (2) of $p_2 = \frac{1}{2}$ atmosphere, and which, therefore, contains carbonic acid, if the concentration of carbonic acid in water is $K_1 = 0{\cdot}04354$ times the pressure of the carbon dioxide in atmospheres, and the first and second dissociation-constants of carbonic acid in water are $K_2 = 3{\cdot}04 \times 10^{-7}$ and $K_3 = 1{\cdot}3 \times 10^{-14}$ respectively?

SOLUTION 244.—In the case of all solutions which are saturated with $CaCO_3$ the equation $[Ca\cdot\cdot]\,[CO_3'']$ = L must be satisfied, where L is the solubility-product of calcium carbonate. In pure aqueous solutions we may assume that the ionic dissociation is complete, and can, therefore, put $[Ca\cdot\cdot]$ = $[CO_3''] = S$. We thus obtain

$$(1)\quad [Ca\cdot\cdot]\,[CO_3''] = L = S^2.$$

By the addition of free carbonic acid the solubility of calcium carbonate is increased, i.e. the concentration of the $Ca\cdot\cdot$-ions is increased owing to the diminution of the CO_3''-ion concentration by the reaction

$$CO_3'' + H_2CO_3 = 2HCO_3',$$

or, in other words, owing to the formation of bicarbonate. The mass-action equation for this reaction is

$$(2)\quad \frac{[HCO_3']^2}{[CO_3'']\,[H_2CO_3]} = K.$$

This constant K may be calculated as follows, from the given values of the dissociation-constants of carbonic acid. For the first dissociation of carbonic according to the equation $H_2CO_3 = H^{\cdot} + HCO_3'$, the law of mass-action gives

$$(3) \quad \frac{[H^{\cdot}]\,[HCO_3']}{[H_2CO_3]} = K_2,$$

and for the second dissociation according to the equation $HCO_3' = H^{\cdot} + CO_3''$ we obtain similarly

$$(4) \quad \frac{[H^{\cdot}]\,[CO_3'']}{[HCO_3']} = K_3.$$

(3) divided by (4) gives (2), thus

$$\frac{[HCO_3']^2}{[CO_3'']\,[H_2CO_3]} = K = \frac{K_2}{K_3}.$$

By multiplying (1) by (2) we obtain

$$(5) \quad \frac{[Ca^{\cdot\cdot}]\,[HCO_3']^2}{[H_2CO_3]} = S^2 \times \frac{K_2}{K_3}.$$

The law of electro-neutrality requires

$$2[Ca^{\cdot\cdot}] + [H^{\cdot}] = [HCO_3'] + 2[CO_3''].$$

Since carbonic acid is a very weak acid, $[H^{\cdot}]$ is very small even in presence of free H_2CO_3, and $[CO_3'']$ may be neglected in comparison with $[HCO_3']$. We thus obtain

$$2[Ca^{\cdot\cdot}] = [HCO_3'].$$

The concentration of $Ca^{\cdot\cdot}$-ions, and, therefore, the solubility of calcium carbonate in water containing carbonic acid, may be calculated from equation (5) if the concentration of the free carbonic acid, $[H_2CO_3]$, in the solution is known. This may be obtained with the help of the factor of proportionality K_1, which is given. If the partial pressure of the CO_2 over the solution is p, then

$$[H_2CO_3] = K_1 p.$$

Substituting this value of $[H_2CO_3]$ in equation (5), and bearing in mind that $2[Ca^{\cdot\cdot}] = [HCO_3']$, we obtain from (5),

$$[Ca^{\cdot\cdot}]^3 = \frac{S^2 K_1 K_2 p}{4K_3},$$

and

$$[Ca\cdot\cdot] = \sqrt[3]{\frac{S^2K_1K_2p}{K_3}}$$

$$= \sqrt[3]{\frac{(1\cdot3)^2\times10^{-8}\times4\cdot354\times10^{-2}\times3\cdot04\times10^{-7}}{4\times1\cdot3\times10^{-11}}\,p}$$

$$= 0\cdot016\sqrt[3]{p}.$$

For $p_1 = \frac{1}{30}$ atmosphere

$[C_a\cdot\cdot] = 0\cdot016\times0\cdot37 = \mathbf{0\cdot0059}$ gram-molecule per litre,

and for $p_2 = \frac{1}{2}$ atmosphere

$[C_a\cdot\cdot] = 0\cdot016\times0\cdot794 = \mathbf{0\cdot0127}$ gram-molecule per litre.

Hydrolysis of Salts

In an aqueous solution of a salt BA of a weak acid HA and a strong base BOH the salt is more or less hydrolysed according to the equation

$$BA + H_2O = HA + BOH.$$

Let x be the degree of hydrolysis, that is, of each gram-molecule of salt in solution let the fraction x be hydrolysed according to the above equation; the fraction $(1 - x)$ of each gram-molecule remains, therefore, unhydrolysed. If c is the total concentration of the salt in gram-molecules per litre, the concentration of HA and of BOH is, therefore, xc, since they are produced in equivalent amounts, and the concentration of the unhydrolysed salt BA is $(1 - x)c$. We shall assume further that the strong electrolytes, the salt BA and the base BOH, are completely dissociated, whilst the weak electrolyte, the acid HA, is practically undissociated, a condition which will be very approximately fulfilled, since the dissociation of the weak acid into H·- and A′-ions, which is feeble even in a pure aqueous solution, will be still further diminished by the presence of the large excess of A′-ions derived from the dissociation of the salt BA. If the concentrations of the various molecules and ions are denoted by square brackets, we may, therefore, put

$$[HA] = xc,\ [OH'] = xc \text{ and } [A'] = (1 - x)c,$$

since, in the last case, the concentration of the A′-ions derived from the dissociation of the HA must, for the reasons given above, be practically negligible. The concentration of the H·-ions, [H·], we obtain from the fact that in any aqueous

solution at a given temperature the product of the concentrations of the H·- and OH′-ions must be constant, or

$$[\mathrm{H}\cdot][\mathrm{OH}'] = K_w$$

K_w is called the ionic product of water. We obtain, therefore

$$[\mathrm{H}\cdot] = \frac{K_w}{[\mathrm{OH}']} = \frac{K_w}{xc}.$$

Applying the law of mass-action to the dissociation of the weak acid HA we obtain

$$K_a = \frac{[\mathrm{H}\cdot][\mathrm{A}']}{[\mathrm{HA}]} = \frac{\frac{K_w}{xc}(1-x)c}{xc} = K_w\left(\frac{1-x}{x^2c}\right),$$

where K_a is the dissociation-constant of the acid. Hence

$$(21)\quad K_H = \frac{K_w}{K_a} = \frac{x^2c}{1-x} = \frac{(xc)(xc)}{(1-x)c}.$$

K_H is called the hydrolysis-constant of the salt BA and, as is evident from equation (21),

$$K_H = \frac{(\text{conc. of free acid})(\text{conc. of free base})}{(\text{conc. of unhydrolysed salt})}.$$

If K_H and, therefore, the degree of hydrolysis x, is very small, that is, if K_a is very much greater than K_w, we may put $(1-x) = 1$ without great error, and we obtain from (21) the approximation formula

$$(22)\quad K_H = x^2c.$$

In an exactly similar way it may be shown that for a salt BA of a weak base BOH and a strong acid HA,

$$(23)\quad K_H = \frac{K_w}{K_b} = \frac{x^2c}{1-x},$$

where K_H is the hydrolysis-constant of the salt, K_b the dissociation-constant of the weak base, x the degree of hydrolysis of the salt and c the total concentration of the salt.

If the salt BA of the weak acid HA and the weak base BOH is hydrolysed according to the equation

$$\mathrm{BA} + \mathrm{H_2O} = \mathrm{HA} + \mathrm{BOH}$$

and if we assume that the dissociation of the unhydrolysed salt (a strong electrolyte) is complete, whilst the weak acid

and base are practically undissociated in presence of the excess of A· and B′-ions furnished by the dissociation of the salt, then if c molecules per litre is the total concentration of BA, and x is the degree of hydrolysis,

$$[A\cdot] = (1 - x)c,\ [B'] = (1 - x)c,\ [HA] = xc,\ [BOH] = xc,$$

where the square brackets denote the concentrations of the enclosed substances in gram-molecules per litre. Therefore

$$K_a = \frac{[H\cdot][A']}{[HA]} = \frac{[H\cdot](1 - x)c}{xc}$$

$$K_b = \frac{[B\cdot][OH']}{[BOH]} = \frac{(1 - x)c[OH']}{xc}$$

and

$$K_a \times K_b = \frac{[H\cdot](1 - x)c}{xc} \times \frac{[OH'](1 - x)c}{xc}$$

$$= \frac{(1 - x)^2[H\cdot][OH']}{x^2} = \frac{(1 - x)^2 K_w}{x^2}.$$

Therefore

$$(24)\ K_H = \frac{K_w}{K_a \times K_b} = \frac{x^2}{(1 - x)^2}$$

$$= \frac{(\text{conc. of free acid})(\text{conc. of free base})}{(\text{conc. of unhydrolysed salt})^2}.$$

Since the concentration c does not appear in this equation the degree of hydrolysis of a salt of a weak acid and a weak base is independent of the concentration.

Hydrolysis—Examples

PROBLEM 245.—At 25° C. the dissociation-constant of ammonia in aqueous solution is $K_b = 1{\cdot}8 \times 10^{-5}$, and at the same temperature the ionic product of water is $K_w = 0{\cdot}8 \times 10^{-14}$. The concentration of hydrogen ions in a solution, which is $c_1 = 0{\cdot}01$ N with respect to ammonia and $c_2 = 0{\cdot}02$ N with respect to diketotetrahydrothiazole, is $a = 1{\cdot}7 \times 10^{-7}$ gram-ion per litre. What is the dissociation-constant K_a of the acid, diketotetrahydrothiazole, and to what degree per cent. is the neutral ammonium salt of the acid hydrolysed (*1*) in a $c_3 = 0{\cdot}001$ N-solution, and (*2*) in a $c_4 = 0{\cdot}1$ N-solution?

SOLUTION 245.—The acid, diketotetrahydrothiazole, may,

for brevity, be represented by the formula AH, in which H is the acid hydrogen or cation, and A the acid radical or anion.

According to the law of mass-action, the equilibrium equations for the dissociation of the base, NH_4OH, and of the acid, AH, are

$$(1)\ \frac{[NH_4\cdot]\,[OH']}{[NH_4OH]} = K_b$$

and

$$(2)\ \frac{[A']\,[H\cdot]}{[AH]} = K_a.$$

For the dissociation of water the ionic product is

$$(3)\ [H\cdot]\,[OH'] = K_w.$$

In an aqueous solution containing both the base and the acid, all three equations must be simultaneously satisfied. In these equations K_a and the concentrations $[OH']$, $[NH_4\cdot]$, $[NH_4OH]$, $[A']$ and $[AH]$ are unknown, whilst $[H\cdot]$ is given $= a$. For the evaluation of these six unknowns three further equations are, therefore, required. These are

$$(4)\ [NH_4\cdot] + [NH_4OH] = c_1,$$

$$(5)\ [A'] + [AH] = c_2$$

$$\text{and } (6)\ [NH_4\cdot] + [H\cdot] = [A'] + [OH'].$$

The concentration of the undissociated salt molecules, $[NH_4A]$, may be neglected, since the salt may be regarded as practically completely dissociated. The problem is, therefore, capable of solution, and its solution is simplified by the fact that $[H\cdot] = a$ is very small compared with c_1 and c_2; the anions A′ are, therefore, derived practically entirely from the dissociation of the salt NH_4A, and the the excess of the acid AH is only slightly dissociated.

Equation (6) therefore simplifies to

$$(7)\ [NH_4\cdot] = [A'].$$

From (1) and (3) we obtain

$$\frac{[NH_4\cdot]}{[NH_4OH]} = \frac{K_b}{[OH']} = \frac{K_b[H\cdot]}{K_w} = \frac{1{\cdot}8 \times 10^{-5} \times 1{\cdot}7 \times 10^{-7}}{0{\cdot}8 \times 10^{-14}}$$

$$= \frac{382}{1}.$$

$[NH_4OH]$ may, therefore, be neglected in comparison with $[NH_4\cdot]$. We thus obtain

from (7) and (4) : $[NH_4^{\cdot}] = [A'] = c_1 = 0{\cdot}01$,

from (5) : $[AH] = c_2 - c_1 = 0{\cdot}01$,

and from (2) : $K_a = \dfrac{(0{\cdot}01)\,[H^{\cdot}]}{(0{\cdot}01)} = [H^{\cdot}] = a = 1{\cdot}7 \times 10^{-7}$.

In a c_3 N-solution of the neutral ammonium salt let the fraction x be hydrolysed according to the equation

$$NH_4A + H_2O = AH + NH_4OH.$$

Then $[NH_4OH] = [AH] = xc_3$,

and $[NH_4^{\cdot}] = [A'] = c_3 - xc_3$.

The ions $H^{\cdot}$ and OH' are present only in very small concentration, since both the base and the acid are very weak; and the concentration of the undissociated salt molecules, $[NH_4A]$, may again be neglected on account of the practically complete dissociation of the salt.

From (1) we thus obtain

$$(8)\quad \frac{c_3(1-x)}{c_3x}\,[OH'] = K_b,$$

and from (2)

$$(9)\quad \frac{c_3(1-x)}{c_3x}\,[H^{\cdot}] = K_a.$$

(8) × (9) gives

$$\frac{(1-x)^2}{x^2}\,[OH']\,[H^{\cdot}] = K_b K_a,$$

and by dividing this result by (3) we obtain

$$\frac{(1-x)^2}{x^2} = \frac{K_bK_a}{K_w},$$

$$\text{and } \frac{1-x}{x} = \sqrt{\frac{K_bK_a}{K_w}},$$

$$\therefore x = \frac{1}{1+\sqrt{\dfrac{K_bK_a}{K_w}}} = \frac{1}{1+\sqrt{\dfrac{1{\cdot}8 \times 1{\cdot}7 \times 10^{-12}}{0{\cdot}8 \times 10^{-14}}}} = \frac{1}{1+\sqrt{382}}$$

$$= 0{\cdot}049.$$

The degree of hydrolysis is, therefore, 4·9 per cent., and is the same for all concentrations of the neutral salt, since x is independent of the total concentration c_3. The degree of

hydrolysis of a salt of a weak acid and a weak base is, therefore, independent of the concentration.

PROBLEM 246.—At 25° the distribution-coefficient of aniline between benzene and water is 10·1. A litre of 0·03138 N-aniline hydrochloride was shaken with 59 c.c. of benzene. After equilibrium was established 50 c.c. of the benzene was found to contain 0·02916 gram of aniline. Calculate (*a*) the hydrolysis-constant of aniline hydrochloride, (*b*) the percentage hydrolysis in 0·1 N-solution and (*c*) the dissociation-constant of aniline as a base, given that the ionic-product for water at 25° is $1{\cdot}2 \times 10^{-14}$.

SOLUTION 246.—(*a*) The molecular weight of aniline is 93, therefore

(1) 50 c.c. of benzene contain $\frac{0{\cdot}02916}{93}$ gram-equivalent of aniline, and the concentration of the aniline in benzene is

$$\frac{0{\cdot}02916}{93} \times \frac{1000}{50} \text{ gram-equivalent per litre.}$$

Since

$$\frac{\text{concentration of aniline in benzene}}{\text{concentration of aniline in water}} = 10{\cdot}1$$

we obtain

(2) concentration of free aniline in water layer

$$= \frac{\text{concentration in benzene}}{10{\cdot}1} = \frac{0{\cdot}02916 \times 1000}{93 \times 50 \times 10{\cdot}1}$$

$$= 0{\cdot}000621 \text{ gram-equiv. per litre.}$$

The total concentration of aniline originally present in the water was 0·03138 gram-equiv. per litre, but, from (1), of this amount 59 c.c. of benzene extracted

$$\frac{0{\cdot}02916}{93} \times \frac{59}{50} = 0{\cdot}00037 \text{ gram-equiv.}$$

The total concentration of aniline (free and combined as hydrochloride) in the water layer at equilibrium is, therefore,

$$0{\cdot}03138 - 0{\cdot}00037 = 0{\cdot}03101 \text{ gram-equiv. per litre.}$$

From (2), however, the concentration of the free aniline is 0·000621 gram-equiv. per litre, therefore the concentration of the aniline hydrochloride is

(3) $0{\cdot}03101 - 0{\cdot}000621 = 0{\cdot}03039$ gram-equiv. per litre.

Since the benzene extracts only aniline and not hydrochloric acid or aniline hydrochloride from the aqueous layer, the total concentration of HCl in the aqueous layer at equilibrium is equal to that of the aniline hydrochloride originally present, namely 0·03138 gram-equiv. per litre. Of this amount, however, 0·03039 gram-equiv. exists as aniline hydrochloride (from (3)), therefore the concentration of free HCl at equilibrium is

$$0{\cdot}03138 - 0{\cdot}03039 = 0{\cdot}00099 \text{ gram-equiv. per litre.}$$

From (**21**)

$$K_H = \frac{\text{(conc. of free acid) (conc. of free base)}}{\text{(conc. of unhydrolysed salt)}}$$

$$= \frac{(0{\cdot}00099)(0{\cdot}000621)}{(0{\cdot}03039)} = \mathbf{2{\cdot}02 \times 10^{-5}}.$$

(*b*) If x is the degree of hydrolysis in 0·1 N-solution, from (**21**)

$$K_H = \frac{x^2 c}{1 - x} \text{ or } 2{\cdot}02 \times 10^{-5} = \frac{0{\cdot}1x^2}{1 - x}$$

$$\therefore \mathbf{x = 1{\cdot}41 \times 10^{-2}}$$

$$= \mathbf{1{\cdot}41} \text{ per cent.}$$

(*c*) From (**21**) $K_H = \dfrac{K_w}{K_b}$

$$\therefore \mathbf{K_b = \frac{K_w}{K_H} = \frac{1{\cdot}2 \times 10^{-14}}{2{\cdot}02 \times 10^{-5}} = 5{\cdot}93 \times 10^{-10}}.$$

Problems for Solution

In the following problems the answers to those marked * have been obtained by using the simplified formulæ (**12**) and (**13**), i.e. by putting $(1 - \alpha) = 1$, and (**22**), i.e. by putting $(1 - x) = 1$.

Faraday's Laws

PROBLEM 247.—A current passed through a water voltameter liberated in 4 minutes 50 c.c. of hydrogen at 17° C. and 750 mm. Calculate the mean current during the whole time.

Ans. 1·669 amp.

PROBLEM 248.—In the preparation of NaOH by the electrolysis of a sodium chloride solution, 600 c.c. of solution containing 40 grams NaOH per litre was obtained after a certain

time. During the same time 30·4 grams of Cu had been deposited in a copper voltameter in series with the electrolytic cell. Calculate the percentage of the theoretical yield of NaOH obtained.

Ans. 62·8 per cent.

PROBLEM 249.—What volume of hydrogen at 18° and 737 mm. is liberated by passing a current of 1·54 amp. through a solution of dilute H_2SO_4 for 2 minutes?

Ans. 23·56 c.c.

PROBLEM 250.—A current of 1·5 amp. is passed through a solution of $CuCl_2$ for 1 hour. What weight of electrolyte is decomposed?

Ans. 3·764 grams.

Transport Numbers

PROBLEM 251.—A solution of $AgNO_3$ containing 1·139 mg. of silver per gram of solution was electrolysed between silver electrodes and the anode liquid after electrolysis contained 39·66 mg. silver in 20·09 grams of solution. In a silver voltameter in series with the electrolytic cell 32·10 mg. of silver was deposited. Calculate the transport numbers of $Ag^{\cdot}$ and NO'_3.

Ans. $Ag^{\cdot} = 0{\cdot}476$, $NO'_3 = 0{\cdot}524$.

PROBLEM 252.— A solution of $CuSO_4$ containing 1 gram $CuSO_4$ per 41·59 grams water was electrolysed between a copper anode and a platinum cathode, a silver voltameter being placed in series with the electrolytic cell. After electrolysis 54·706 grams of the cathode solution gave on analysis 0·5118 gram CuO. During the electrolysis 0·6934 gram of silver was deposited in the voltameter. Calculate the transport numbers of SO''_4 and $Cu^{\cdot\cdot}$. (Cu = 63·6, S = 32·06, O = 16, Ag = 107·9.)

Ans. $SO''_4 = 0{\cdot}5146$, $Cu^{\cdot\cdot} = 0{\cdot}4854$.

PROBLEM 253.—A solution of NaCl containing 0·01784 per cent. of chlorine was electrolysed between a Cd anode and a Pt cathode, with a silver voltameter in series. After electrolysis the solution was divided into three portions, cathode, anode, and middle portion. The concentration of the latter was unchanged, whilst 226·99 grams of anode solution contained 0·04679 gram chlorine, and 331·49 grams cathode solution contained 0·05302 gram chlorine. In the silver

voltameter the equivalent of 0·01021 gram chlorine was deposited. Calculate the transport numbers of Cl′ and Na·.

Ans. Cl′ = 0·611, Na· = 0·389.

PROBLEM 254.—A solution of $CdCl_2$ containing 0·2016 per cent. of chlorine was electrolysed between a Cd anode and a Pt cathode. After electrolysis 33·59 grams of the anode liquid contained 0·08020 gram Cl and 54·12 grams of the cathode liquid contained 0·09662 gram Cl. The concentration of the middle portion was unchanged. In a silver voltameter in series with the electrolytic cell 0·06662 gram of silver was deposited during the electrolysis. Calculate the transport numbers of Cl′ and Cd··.

Ans. Cl′ = 0·570, Cd·· = 0·430.

Electrolytic Dissociation

PROBLEM 255.—The equiv. conductivity of LiCl at 18° is 101·4 r.o. at infinite dilution and 93·6 r.o. for a 0·01 N-solution. What is the degree of dissociation and the concentration of the Cl′ ions in this solution?

Ans. $\alpha = 0{\cdot}923$, [Cl′] = 0·00923 gram-ion/litre.

PROBLEM 256.—At 18° the equiv. conductivity of HI at infinite dilution is 384 r.o. and the specific conductivity of a 0·405 N-solution is 0·1332 r.o. What is the concentration of the H·-ions in this solution?

Ans. [H·] = 0·347 gram-ion/litre.

PROBLEM 257.—The equiv. conductivity at 25° of acetic acid containing 1 gram-equiv. in 32 litres is 9·2 r.o. The equiv. conductivity at infinite dilution is 389 r.o. Find the dissociation-constant of the acid.

Ans. $1{\cdot}79 \times 10^{-5}$.

PROBLEM 258.—At 25° the specific conductivity of butyric acid at a dilution of 64 litres is $1{\cdot}812 \times 10^{-4}$ r.o. The equiv. conductivity at infinite dilution is 380 r.o. What is the degree of dissociation and the concentration of H·-ions in the solution, and the dissociation-constant of the acid?

Ans. $\alpha = 0{\cdot}0305$, [H·] = $4{\cdot}765 \times 10^{-4}$ gram-ions/litre,

$K = 1{\cdot}5 \times 10^{-5}$.

PROBLEM 259 (cf. preceding problem).—What is the value of the dissociation-constant of butyric acid if the concentra-

tion is measured in gram-equivalents per c.c. instead of gram-equivalents per litre?

Ans. $1{\cdot}5 \times 10^{-8}$.

PROBLEM 260.—The specific conductivity of a 5 per cent. (by weight) $BaCl_2$ solution is 389×10^{-4} r.o. and its density 1·0445 at 18°. What is the equivalent conductivity and degree of dissociation of the solution, if the equiv. conductivity of $BaCl_2$ at infinite dilution is 123 r.o. at 18°?

Ans. $\Lambda = 77{\cdot}7$, $\alpha = 0{\cdot}632$.

PROBLEM 261 (cf. preceding problem).—What is the freezing-point of the $BaCl_2$ solution?

Ans. $-1{\cdot}064°$.

PROBLEM 262.—At 25° the specific conductivity of ammonia solutions, containing c gram-equivs. per litre is κ r.o. The ionic conductivity of the NH_4·-ion at this temperature is 70·4 and of the OH′-ion 200·6. Calculate the equiv. conductivity and degree of dissociation at each concentration and the mean dissociation-constant.

c	κ
0·0109	$1{\cdot}220 \times 10^{-4}$
0·0219	$1{\cdot}730 \times 10^{-4}$

Ans. $\Lambda = 11{\cdot}2$ and 7·9 r.o., $\alpha = 0{\cdot}0413$ and 0·0291, $K = 1{\cdot}94 \times 10^{-5}$ and $1{\cdot}92 \times 10^{-5}$, mean $= 1{\cdot}93 \times 10^{-5}$.

* PROBLEM 263 (cf. preceding problem).—At what concentration is ammonia 1 per cent. dissociated in solution?

Ans. $c = 0{\cdot}193$ N.

PROBLEM 264.—At 25° the specific conductivity of ethylamine at a dilution of 16 litres is $1{\cdot}312 \times 10^{-3}$ r.o., the equiv. conductivity at infinite dilution is 232·6 r.o. Calculate the dissociation-constant.

Ans. $5{\cdot}6 \times 10^{-4}$.

PROBLEM 265 (cf. preceding problem).—What is the concentration of OH′-ions in the ethylamine solution?

Ans. $5{\cdot}64 \times 10^{-3}$ gram-ion/litre.

PROBLEM 266.—At what concentration of ethylamine is the concentration of the OH′-ions 0·01 N?

Ans. $c = 0{\cdot}1886$ mole/litre.

PROBLEM 267.—At 25° the dissociation-constant of mono-

chloracetic acid is $1{\cdot}55 \times 10^{-3}$, and its equiv. conductivity at a dilution of 32 litres is 77·2 r.o. What is its equiv. conductivity at infinite dilution?

Ans. 388 r.o.

* PROBLEM 268.—At 25° the dissociation-constant of lactic acid is $1{\cdot}4 \times 10^{-4}$ and of monochloracetic acid $1{\cdot}55 \times 10^{-3}$. At what concentrations of lactic and chloracetic acids is the H·-ion concentration = 0·01 N?

Ans. For lactic, $c = 0{\cdot}724$ N.
For chloracetic, $c = 0{\cdot}0745$ N.

PROBLEM 269.—The specific conductivity of KCl is practically proportional to its concentration in solutions of moderate concentration. The specific conductivity at 18° of a 10 per cent. KCl solution is 0·1359 r.o. and of a 15 per cent. solution 0·2020 r.o. What is the percentage concentration of a KCl solution of which the specific conductivity is 0·1640 r.o.?

Ans. 12·13 per cent.

PROBLEM 270.—The density at 0° of a $Ca(NO_3)_2$ solution containing 0·208 gram-molecule per litre is 1·010. Its freezing-point is − 0·910° and its molecular conductivity at 0° is 78·8 r.o. Taking the molecular conductivity at infinite dilution = 129 r.o. at 0° and the freezing-point constant for water = 1·86 (gram-mole in 1000 grams water), calculate the degree of dissociation from the conductivity and from the freezing-point.

Ans. From conductivity = 0·611.
From freezing-point = 0·648.

PROBLEM 271.—At 25° the specific conductivities of KCl and LiCl at a dilution of 32 litres are $4{\cdot}25 \times 10^{-3}$ r.o. and $3{\cdot}243 \times 10^{-3}$ r.o. respectively. Compare the degrees of dissociation of the two salts at this dilution, taking the ionic conductivities of K, Li and Cl at 25° as 75·3, 41 and 76 r.o. respectively.

Ans. KCl = 0·899, LiCl = 0·892.

* PROBLEM 272.—The dissociation-constant of acetic acid at 18° is $1{\cdot}8 \times 10^{-5}$. Calculate the degree of dissociation and the H·-ion concentration (1) in a 0·25 N-acetic acid solution, (2) in a 0·25 N-acetic acid solution containing 0·25 N-sodium acetate, if the sodium acetate is assumed to be completely dissociated.

Ans. (1) $\alpha = 8{\cdot}48 \times 10^{-3}$, $[H^{\cdot}] = 2{\cdot}12 \times 10^{-3}$ gram-ion/litre,
(2) $\alpha = 7 \times 10^{-4}$, $[H^{\cdot}] = 1{\cdot}75 \times 10^{-4}$ gram-ion/litre.

PROBLEM 273.—At 18° the specific conductivity of a 5 per cent. solution of $Mg(NO_3)_2$ is 438×10^{-4} r.o. and its density 1·0378. What is its degree of dissociation if the equivalent conductivity of $Mg(NO_3)_2$ at infinite dilution is 109·8 r.o.?

Ans. 0·57.

PROBLEM 274.—At 18° the molecular conductivity of $LiNO_3$ is 94·46 r.o. at infinite dilution, and 75·01 r.o. in a 0·2 N-solution. What is the concentration of $Li^{\cdot}$-ions in this solution?

Ans. 0·159 N.

PROBLEM 275.—The density of a 5 per cent. NaCl solution at 18° is 1·0345 and its specific conductivity 672×10^{-4} r.o. What is (1) the molecular conductivity, (2) the degree of dissociation of the solution, if the molecular conductivity of NaCl at infinite dilution is 109 r.o.? (3) What is the vapour-pressure of the solution at 18° if that of pure water is 15·33 mm.?

Ans. (1) 76 r.o., (2) 0·697, (3) 14·91 mm.

PROBLEM 276.—The velocity of migration of the $Ag^{\cdot}$-ion at 18° is 0·000577 cms. per sec. and of the NO'_3-ion 0·000630 cms. per sec. The specific conductivity of 0·1 N-$AgNO_3$ at 18° is 0·00947 r.o. What is the degree of dissociation of the $AgNO_3$?

Ans. 81·3 per cent.

PROBLEM 277.—The freezing-point of a 0·1 molecular N – $CaCl_2$ solution is – 0·482°. (1) Calculate the degree of dissociation (freezing-point constant = 1·89 for gram-mol. per litre). (2) Compare the value with that found from the equivalent conductivity at 18°, which is 82·79 r.o., whilst the equivalent conductivity of $CaCl_2$ at infinite dilution is 115·8 r.o.

Ans. (1) 0·775, (2) 0·715.

*PROBLEM 278.—What is the concentration of $H^{\cdot}$-ions in a solution containing 1 gram-molecule of acetic acid and 1 gram-molecule of cyanacetic acid per litre? The dissociation-constant of acetic acid is $1{\cdot}8 \times 10^{-5}$ and of cyanacetic acid 370×10^{-5}.

Ans. $6{\cdot}1 \times 10^{-2}$ N.

PROBLEM 279.—The molecular conductivity at 25° of ethyl hydrogen malonate is 356 at infinite dilution, and 21·5, 41·9 and 57·3 at the dilutions 8·57, 34·28 and 68·56 litres respectively. Calculate the degree of dissociation and the dissociation-constant at each dilution.

Ans. α = 6·04, 11·8 and 16·1 per cent.

$K = 4{\cdot}54 \times 10^{-4}$, $4{\cdot}58 \times 10^{-4}$ and $4{\cdot}51 \times 10^{-4}$.

PROBLEM 280.—At 25° the molecular conductivities of malonic acid at the dilutions 32, 64 and 128 litres are 77·1, 103·6 and 137·0 r.o. respectively. The molecular conductivity at infinite dilution for dissociation into H·- and $C_3H_3O'_4$-ions is 382 r.o. Calculate the degree of dissociation and the dissociation-constant at each dilution. What conclusion may be drawn from these figures as to the manner in which malonic acid dissociates at these dilutions?

Ans. α = 0·202, 0·271, 0·359

$K = 1{\cdot}59 \times 10^{-3}$, $1{\cdot}58 \times 10^{-3}$, $1{\cdot}57 \times 10^{-3}$.

PROBLEM 281 (cf. preceding problem).—For the dilutions 256, 512, 1024 and 2048 litres the molecular conductivities of malonic acid at 25° are 176·8, 222·6, 269·9, and 313·9 respectively. What conclusions may be drawn from the values of K calculated from Ostwald's dilution law as to the dissociation of the acid at these dilutions?

Ans. $K = 1{\cdot}57, 1{\cdot}62, 1{\cdot}68, 1{\cdot}87 \times 10^{-3}$, ∴ second dissociation begins to be appreciable after *ca.* 256 litres.

PROBLEM 282.—A solution of NaCl containing 0·0585 gram per 100 c.c. freezes at − 0·03674°. The equiv. conductivity of NaCl at infinite dilution is 109 r.o. Assuming the degree of dissociation at 18° to be the same as at 0°, calculate the specific conductivity of the above solution. Take freezing-point constant = 1·89 for gram-molecule per litre.

Ans. $1{\cdot}029 \times 10^{-3}$ r.o.

PROBLEM 283.—At 18° the molecular conductivity of boric acid at the dilution v litres per gram-molecule is μ r.o.

v	11·1	22·2	33·3
μ	0·0474	0·0670	0·0825

Calculate the degree of dissociation and dissociation-constant at each dilution, given that the molecular conductivity at infinite dilution for dissociation into H·- and $H_2BO'_3$-ions is 346 r.o.

Ans. $\alpha = 1{\cdot}37 \times 10^{-4}, 1{\cdot}94 \times 10^{-4}, 2{\cdot}39 \times 10^{-4}$
$K = 1{\cdot}70 \times 10^{-9}, 1{\cdot}69 \times 10^{-9}, 1{\cdot}71 \times 10^{-9}$.

PROBLEM 284.—The specific conductivity of a 0·509 N-KNO_3 solution at 18° is 454×10^{-4} r.o. The temperature-coefficient of the specific conductivity between 18° and 22° is 0·0208. What is the equivalent conductivity of the solution at 20°?

Ans. 92·9 r.o.

PROBLEM 285.—At 25° the specific conductivity of malic acid at a dilution of 32 litres is $1{\cdot}263 \times 10^{-3}$ r.o. The equivalent conductivity at infinite dilution for dissociation into H·- and $C_4H_5O'_5$-ions is 380 r.o. Calculate the degree of dissociation and the dissociation-constant.

Ans. $\alpha = 0{\cdot}106$, $K = 3{\cdot}93 \times 10^{-4}$.

PROBLEM 286 (cf. preceding problem).—At what dilution is the concentration of H·-ions in a solution of malic acid 0·02 N?

Ans. 0·963 litre.

PROBLEM 287.—At 25° the equivalent conductivities of fumaric and maleic acids at a dilution of 32 litres are 60·1 and 179 r.o. respectively. The equivalent conductivities at infinite dilution for dissociation into two ions are 385·6 and 391·8 r.o. respectively. Compare their dissociation-constants.

Ans. Fumaric 9×10^{-4}, maleic $1{\cdot}2 \times 10^{-2}$.

PROBLEM 288.—The molecular conductivity of a $Ca(NO_3)_2$ solution containing 1 gram-molecule in 23·81 litres is 98·9 r.o. at 0°. The molecular conductivity at infinite dilution is 129·2 r.o. at 0°. What is the freezing-point of the solution? Take freezing-point constant = 1·89 for gram-mole/litre.

Ans. − 0·2008°.

PROBLEM 289.—The specific conductivity of 0·135 N-propionic acid at 18° is $4{\cdot}79 \times 10^{-4}$ r.o. and that of 0·001 N-sodium propionate is $7{\cdot}54 \times 10^{-5}$ r.o. The ionic conductivity of the Na·-ion is 44·4 and of the H·-ion 318 r.o. Assuming the sodium propionate to be completely dissociated, calculate the dissociation constant of propionic acid.

Ans. $1{\cdot}41 \times 10^{-5}$.

* PROBLEM 290 (cf. preceding problem).—The dissociation-constant of benzoic acid is 6×10^{-5}. What is the ratio of

the H·-ion concentrations in benzoic and propionic acids at equal dilutions?

Ans. 2·07 : 1.

PROBLEM 291 (cf. preceding problem).—At what dilution is the concentration of H·-ions in a benzoic acid solution 0·005 N?

Ans. 2·37 litres.

PROBLEM 292.—The velocity-constant for the inversion of cane sugar by 0·0125 N-HCl at 54° is 0·00469. The velocity-constant for inversion by 0·25 N-formic acid at the same temperature is 0·00255. Calculate the dissociation-constant of formic acid, if it is assumed that the velocity-constant is proportional to the H·-ion concentration, and that the HCl is completely dissociated.

Ans. $K = 1{\cdot}9 \times 10^{-4}$.

PROBLEM 293 (cf. preceding problem).—What would be the velocity-constant at 54° for inversion by a 0·25 N-formic acid solution, containing 0·1 N-sodium formate, if the latter is regarded as completely dissociated?

Ans. 0·000169.

Solubility-Product—Hydrolysis

PROBLEM 294.—At 18° the specific conductivity of a saturated solution of silver chloride in water was $2{\cdot}40 \times 10^{-6}$ r.o., and that of the water used was $1{\cdot}16 \times 10^{-6}$ r.o. Given the equivalent conductivity at infinite dilution of $AgNO_3$ = 116·5 r.o., of NaCl = 110·3 r.o. and of $NaNO_3$ = 105·2 r.o., and on the assumption that the AgCl is completely dissociated in solution, calculate the solubility in gram-molecules per litre and the solubility-product of AgCl at 18°.

Ans. $S = 1{\cdot}018 \times 10^{-5}$ gram-mol./litre, $L = 1{\cdot}035 \times 10^{-10}$.

PROBLEM 295.—At 16·3° a saturated solution of barium oxalate has a specific conductivity of $67{\cdot}7 \times 10^{-6}$ r.o. whilst that of the water used was $1{\cdot}2 \times 10^{-6}$ r.o. The ionic conductivities for $\frac{1}{2}$ $Ba^{\cdot\cdot}$ and $\frac{1}{2}$ $C_2O''_4$ at 16·3° are 50·6 and 58·4 r.o. respectively. On the assumption that the dissociation of the salt is complete, calculate the solubility, in gram-molecules per litre, of BaC_2O_4 at 16·3°.

Ans. $3{\cdot}05 \times 10^{-4}$.

PROBLEM 296.—At 25° the concentration of a saturated solution of silver acetate is 0·0664 gram-molecule per litre. The molecular conductivity of the solution is 75·2 r.o. and the molecular conductivity of silver acetate at infinite dilution is 101·5 r.o. What is the solubility-product of silver acetate?

Ans. 0·00241.

PROBLEM 297. — The solubility of $CaSO_4$ at 20° is 2·036 grams per litre. The specific conductivity of the saturated solution at 20° is 1968×10^{-6} r.o. The ionic conductivity for $\frac{1}{2}$ $Ca^{\cdot\cdot}$ at 18° is 52 r.o. and the temperature-coefficient of the conductivity is 0·0238. The ionic conductivity for $\frac{1}{2}$ SO''_4 at 18° is 68·3 r.o. and the temperature-coefficient 0·0227. Calculate the degree of dissociation of $CaSO_4$ in the saturated solution and the solubility-product at 20°.

Ans. $\alpha = 52{\cdot}25$ per cent., $L = 6{\cdot}11 \times 10^{-5}$.

PROBLEM 298.—The solubility of benzoic acid at 25° is 3·40 grams per litre and its dissociation-constant is 6×10^{-5}. What would be its solubility in a 0·01 N-sodium benzoate solution and in a 0·01 N-HCl solution, if both these substances are regarded as completely dissociated?

Ans. 0·02678 gram-mol. per litre for both.

PROBLEM 299.—Magnesium carbonate, which is practically insoluble in water, dissolves in water containing CO_2 owing to formation of bicarbonate. In a solution saturated with CO_2 under atmospheric pressure the solubility of $MgCO_3$ at 25° was 0·325 gram-molecule per litre. The first dissociation-constant of carbonic acid is $\frac{[H^{\cdot}]\,[HCO'_3]}{[H_2CO_3]} = 3{\cdot}04 \times 10^{-7}$ and the second dissociation-constant is $\frac{[H^{\cdot}]\,[CO''_3]}{[HCO'_3]} = 1{\cdot}295 \times 10^{-11}$.

According to Henry's law the concentration of H_2CO_3 is proportional to the partial pressure of CO_2, the relation at 25° being given by $[H_2CO_3] = 4{\cdot}92 \times 10^{-2}(CO_2)$, if $[H_2CO_3]$ is expressed in gram-molecules per litre and (CO_2) in atmospheres. On the assumption that the whole of the magnesium in the solution is in the form of bicarbonate, and that the bicarbonate is 61 per cent. dissociated, calculate the solubility-product of $MgCO_3$ at 25°. (Express all concentrations in gram-molecules or gram-ions per litre.)

Ans. $2{\cdot}7 \times 10^{-5}$.

PROBLEM 300.—At 25° the molecular conductivity of aniline hydrochloride at a dilution of 256 litres is 130·5. At the same dilution, but in presence of a sufficient excess of aniline to practically prevent hydrolysis, it is 107·1. The conductivity of the aniline in presence of its hydrochloride may be neglected. The equivalent conductivity of HCl at a dilution of 256 litres is 410. Calculate the degree of hydrolysis of aniline hydrochloride at this dilution.

Ans. 7·72 per cent.

PROBLEM 301.—From the degree of hydrolysis obtained in the preceding problem calculate the hydrolysis-constant of aniline hydrochloride, and the dissociation-constant of aniline as a base, given that the ionic product for water at 25° is $1{\cdot}21 \times 10^{-14}$. Assume the aniline hydrochloride and the HCl to be completely dissociated, and the aniline to be practically undissociated.

Ans. $K_H = 2{\cdot}52 \times 10^{-5}$, $K_b = 4{\cdot}8 \times 10^{-10}$.

PROBLEM 302.—From the result obtained in the preceding problem calculate the degree of hydrolysis of aniline hydrochloride in a 0·01 N-solution.

Ans. 4·88 per cent.

PROBLEM 303.—At 20° the specific conductivity of a saturated solution of TlCl is 1680×10^{-6} r.o. The total concentration of TlCl as determined directly at 20° is $1{\cdot}36 \times 10^{-2}$ gram-molecules per litre. The equivalent conductivity of TlCl at infinite dilution is 137·3 r.o. What is the degree of dissociation of a saturated solution of TlCl at 20°, and what is the solubility-product of TlCl?

Ans. $\alpha = 90$ per cent., $L = 1{\cdot}5 \times 10^{-4}$.

PROBLEM 304.—The molecular conductivity of carbonic acid at the dilution of 1 gram-molecule in v litres is μ r.o.

v	27·5	55·0	110·0
μ	1·033	1·450	2·040.

Calculate the degree of dissociation and the dissociation-constant for each dilution for dissociation into $H^{\cdot}$- and HCO'_3-ions, given μ_∞ for $NaHCO_3 = 84{\cdot}9$, for $NaCl = 110{\cdot}3$ and for $HCl = 381{\cdot}9$ r.o.

Ans. $\alpha = 2{\cdot}9 \times 10^{-3}$, $4{\cdot}07 \times 10^{-3}$, $5{\cdot}72 \times 10^{-3}$

$K = 3{\cdot}06 \times 10^{-7}$, $3{\cdot}02 \times 10^{-7}$, $2{\cdot}99 \times 10^{-7}$,

mean $= 3{\cdot}02 \times 10^{-7}$.

* PROBLEM 305.—From the dissociation-constant of carbonic acid obtained in the preceding problem calculate the hydrolysis-constant for the hydrolysis of $NaHCO_3$ according to the equation

$$NaHCO_3 + H_2O = NaOH + H_2CO_3,$$

and the degree of hydrolysis of the salt in 0·1 N-solution. Assume the strong electrolytes to be completely dissociated, and the weak acid to be practically undissociated, and take the ionic product of water $= 1{\cdot}2 \times 10^{-14}$.

Ans. $K = 3{\cdot}97 \times 10^{-8}$, $x = 0{\cdot}063$ per cent.

PROBLEM 306.—At 100° C. 100 c.c. of water dissolve 0·12 gram of AgCNO. How much AgCNO will be dissolved at this temperature by 100 c.c. of a solution containing 1 gram of $AgNO_3$? The silver salts may be regarded as completely ionised.

Ans. 0·016 gram.

PROBLEM 307.—The solubility of Ag_2CO_3 in water at 25° is 1×10^{-4} gram-molecule per litre. Calculate the solubility-product, assuming that the dissociation is complete.

Ans. $[Ag\cdot]^2\,[CO''_3] = 4 \times 10^{-12}$.

PROBLEM 308 (cf. preceding problem).—What is the solubility at 25°, in gram-molecules per litre, of Ag_2CO_3 in 0·1 molecular N-Na_2CO_3 solution. Assume complete dissociation of both salts.

Ans. $3{\cdot}16 \times 10^{-6}$.

PROBLEM 309.—At 25° the solubility of AgCl in water is $1{\cdot}5 \times 10^{-5}$ gram-molecule per litre and that of AgBr 7×10^{-7} gram-molecule per litre. On the assumption that both salts are practically completely dissociated, calculate the concentrations of $Ag\cdot$-, Cl'- and Br'-ions in a solution which at 25° is saturated with both AgCl and AgBr.

Ans. $[Ag\cdot] = 15{\cdot}03 \times 10^{-6}$, $[Cl'] = 15 \times 10^{-6}$,
$[Br'] = 3{\cdot}26 \times 10^{-8}$ gram-ion/litre.

PROBLEM 310.—A solution of $MgCl_2$ was treated with a solution of NH_4OH and the precipitated $Mg(OH)_2$ shaken with the solution till equilibrium was established. The solution on analysis gave 0·0219 gram-molecule $MgCl_2$ per litre, 0·0115 gram-molecule NH_4Cl per litre and 0·0394 gram-molecule of free NH_4OH per litre. The dissociation-constant of NH_4OH is $1{\cdot}8 \times 10^{-5}$. Assuming the $Mg(OH)_2$, $MgCl_2$

and NH_4Cl to be completely dissociated and the NH_4OH in presence of the NH_4Cl to be practically undissociated, calculate the solubility of $Mg(OH)_2$ in water in gram-molecules per litre and its solubility-product.

Ans. $S = 2{\cdot}75 \times 10^{-4}$ gram-mol./litre, $L = 8{\cdot}33 \times 10^{-11}$.

PROBLEM 311.—The solubility of silver hydroxide as determined directly is $2{\cdot}16 \times 10^{-4}$ gram-molecule per litre. The solubility of AgCl as determined by the conductivity method is $1{\cdot}5 \times 10^{-5}$ gram-molecule per litre. A dilute solution of KOH was shaken with an excess of moist silver oxide and silver chloride till equilibrium according to the equation

$$AgCl + KOH = AgOH + KCl$$

was established. The solution then contained 0·666 milligram-molecule of KCl per litre and 70·7 milligram-molecule of KOH per litre. Assuming that the KCl is 95 per cent. and the KOH 90 per cent. dissociated, calculate the solubility-product and degree of dissociation of AgOH in a pure aqueous saturated solution.

Ans. $L = 2{\cdot}26 \times 10^{-8}$, $\alpha = 69{\cdot}6$ per cent.

* PROBLEM 312.—Calculate the percentage hydrolysis of sodium acetate in 0·1 N-solution at 25° from the following data, assuming that the salt is completely dissociated.

Dissociation-constant of acetic acid = 0·000018
Ionic product for water = $1{\cdot}21 \times 10^{-14}$.

Ans. $8{\cdot}2 \times 10^{-3}$ per cent.

PROBLEM 313.—At 25° the velocity-constant for the saponification of methyl acetate by N-HCl containing c gram-molecule of urea per litre is k.

c	0·0	0·5	1·0	2·0
k	0·00315	0·00237	0·00184	0·00114.

Assuming that the velocity-constant is proportional to the concentration of free acid, calculate the hydrolysis-constant of urea hydrochloride for each concentration and the mean value.

Ans. 0·766, 0·820, 0·772, mean 0·786.

PROBLEM 314.—From the mean hydrolysis-constant of urea hydrochloride found in the preceding example, calculate the dissociation-constant of urea into the ions CON_2H_5' and OH'. Take the ionic product of water at 25° = $1{\cdot}2 \times 10^{-14}$

and assume that the free acid and the salt are completely dissociated, whilst the weak base is practically undissociated.

Ans. $K_b = 1{\cdot}53 \times 10^{-14}$.

PROBLEM 315 (cf. problem 162).—The velocity-constant for the decomposition of diacetonealcohol by 0·1 N-NaHS, under the same conditions as in Problem 162, is 0·000037. Taking the degree of dissociation of 0·1 N-NaOH = 90 per cent., calculate the degree of hydrolysis of the 0·1 N-NaHS according to the equation

$$NaHS + H_2O = NaOH + H_2S.$$

Assume that the degree of dissociation of both NaOH and NaHS in the hydrosulphide solution is 90 per cent.

Ans. 0·17 per cent.

*PROBLEM 316 (cf. preceding problem).—What would be the degree of hydrolysis of NaHS in 0·01 N-solution?

Ans. 0·537 per cent.

PROBLEM 317.—At 25° the dissociation-constant of aniline is $4{\cdot}8 \times 10^{-10}$ and of acetic acid $1{\cdot}8 \times 10^{-5}$. The ionic product of water is $1{\cdot}2 \times 10^{-14}$. What is the degree of hydrolysis of 0·01 and 0·05 N-solutions of aniline acetate, if the unhydrolysed aniline acetate is assumed to be completely dissociated?

Ans. 54·12 per cent. for both concentrations.

PROBLEM 318 (cf. preceding problem).—What is the H·-ion concentration in each of the aniline acetate solutions?

Ans. $2{\cdot}12 \times 10^{-5}$ gram-ion per litre in each.

PROBLEM 319.—At 100° the following figures were obtained in the catalysis of N/32 methyl acetate solution by N/500 HCl, A being the titre of 10 c.c. of the solution at the time t,

t	0	64	113	152	∞	minutes
A	1·10	4·15	6·03	7·35	15·70	c.c. N/50 NaOH.

The velocity-constant for the catalysis of N/32 methyl acetate by a solution of $AlCl_3$ containing 1/32 gram-molecule per litre was 0·00216 at 100°. Assuming proportionality between the velocity-constant and the concentration of HCl, calculate the degree of hydrolysis of the $AlCl_3$ solution.

Ans. 8·7 per cent.

PROBLEM 320.—At 100° the following figures were obtained in the catalysis of the inversion of a 7·5 per cent. cane sugar

solution by N/1000 HCl, A being the angle of rotation at the time t,

t	0	22	40	∞ minutes
A	+ 10·66°	+ 2·43°	− 0·49°	− 3·63°.

At 100° the figures for the catalysis of the same sugar solution by an $AlCl_3$ solution containing 1/32 molecule per litre were

t	0	15	26	∞ minutes
A	+ 10·78°	− 0·16°	− 2·36°	− 3·53°.

Assuming proportionality between the velocity-constant and the HCl concentration, calculate the degree of hydrolysis of the $AlCl_3$ solution.

Ans. 8·03 per cent.

PROBLEM 321.—The partition-coefficient of the weak acid hydroxyazobenzene, $C_6H_5N : N . C_6H_4OH$, between benzene and water is 539. 1000 c.c. of an aqueous solution containing 0·01 gram-equivalent of the acid and 0·012 gram-equivalent of $Ba(OH)_2$ was shaken with 60 c.c. of benzene. The concentration of the acid in the benzene layer was found to be 0·0537 gram in 50 c.c. Calculate the hydrolysis-constant of the barium salt and the degree of hydrolysis in a 0·01 equivalent N-solution of the pure salt.

Ans. $K_H = 2·34 \times 10^{-6}$, $*x = 1·53$ per cent.

PROBLEM 322.—At 25° the partition-coefficient of *p*-nitraniline between benzene and water is 9·0. 1000 c.c. of an aqueous solution containing 0·05035 equivalent of HCl and 0·00693 equivalent of the base *p*-nitraniline was shaken with 59 c.c. of benzene till equilibrium was established. 50 c.c. of the benzene solution then contained 0·2165 gram of *p*-nitraniline. Calculate the hydrolysis-constant of *p*-nitraniline hydrochloride and the degree of hydrolysis in a 0·05035 N pure aqueous solution of the salt.

Ans. $K_H = 10·67 \times 10^{-2}$, $x = 74·2$ per cent.

PROBLEM 323.—At 25° the solubility of cinnamic acid in water is 0·00331 gram-molecule per litre, and its dissociation-constant is $3·55 \times 10^{-5}$. The ionic product of water is $1·2 \times 10^{-14}$. The solubility of cinnamic acid in a solution containing 0·01 gram-molecule of aniline per litre is 0·00804 gram-molecule per litre. Assuming the unhydrolysed aniline cinnamate to be 93 per cent. dissociated, calculate the dissociation-constant of aniline.

Ans. $5·02 \times 10^{-10}$.

CHAPTER X

Electromotive Force

ELECTRODE POTENTIAL.—NORMAL POTENTIAL.—CONCENTRATION CELLS.—ELECTROMOTIVE FORCE OF GALVANIC ELEMENTS. — DIFFUSION POTENTIAL. — OXIDATION-REDUCTION POTENTIAL.—AFFINITY OR MAXIMUM WORK OF A REACTION IN A GALVANIC ELEMENT.—GIBBS-HELMHOLTZ EQUATION

Electrode Potential

THE electromotive force of a metal electrode (i.e. one which furnishes only positive ions) against a solution of a salt of the metal is

$$(1)\quad \epsilon = -\frac{RT}{nF}\log_e \frac{P}{p} = -\frac{RT}{nF}\log_e \frac{C}{c}.$$

Here ϵ denotes the potential difference between the metal and the solution, and must be taken with its proper sign. It is positive if the metal is charged positively with respect to the solution and negative if the metal is negatively charged. P is the electrolytic solution pressure (or tension) of the metal, p the osmotic pressure of the metal ions in the solution, and C and c the concentrations of the metal ions in gram-ions per litre, corresponding to the osmotic pressures P and p. n is the valency of the metal ion or the number of gram-equivalents in a gram-ion. F is one faraday or 96540 coulombs, the charge carried by one gram-equivalent of any ion. T is the absolute temperature and R the gas-constant. When ϵ is expressed in volts (i.e. when the unit of energy is the volt-coulomb or joule) the numerical value of R is 8·32. On changing from natural to common logarithms the above expression, therefore, becomes

$$\epsilon = -\frac{8{\cdot}32 \times 2{\cdot}302 \times T}{n \times 96540}\log\frac{P}{p} = -\frac{1{\cdot}984 \times 10^{-4} \times T}{n}\log\frac{P}{p}$$
$$= -\frac{1{\cdot}984 \times 10^{-4} \times T}{n}\log\frac{C}{c}.$$

For a temperature of 18° C. = 291° absolute, $\frac{2{\cdot}032 \times RT}{F}$ is, therefore, 0·0577, and for 25° C. = 298° absolute, it is 0·0591. For ordinary temperatures the value 0·058 may be employed, so that we obtain

$$(2)\quad \epsilon = -\frac{0{\cdot}058}{n}\log\frac{P}{p} = -\frac{0{\cdot}058}{n}\log\frac{C}{c}.$$

For an electrode which furnishes only negative ions (e.g. Cl_2, Br_2, etc.) the corresponding expression is

$$(3)\quad \epsilon = +\frac{0{\cdot}058}{n}\log\frac{P}{p} = +\frac{0{\cdot}058}{n}\log\frac{C}{c}.$$

Normal Potential

The electromotive force, ϵ_o, of an electrode against a solution which is normal with respect to the corresponding ions (i.e. contains 1 gram-ion per litre) is called the normal potential (or electrolytic potential) of the electrode substance. Thus for a metal electrode we obtain from (1), since $c = 1$,

$$(4)\quad \epsilon_o = -\frac{RT}{nF}\log_e C = -\frac{0{\cdot}058}{n}\log C,$$

and, for any other concentration c, from (2)

$$(5)\quad \epsilon = \epsilon_o + \frac{RT'}{nF}\log_e c = \epsilon_o + \frac{0{\cdot}058}{n}\log c.$$

E.M.F. of Concentration Cell

The E.M.F. of a concentration cell of the form

Metal	metal salt solution in which the concentration of the metal ions is c	metal salt solution in which the concentration of the metal ions is c_1	Metal

is

$$E = \epsilon - \epsilon_1$$

if the diffusion potential at the junction of the two solutions is neglected. ϵ is the electrode potential at the junction

Metal/solution of ionic conc. c.

ϵ_1 is the electrode potential at the junction

Metal/solution of ionic conc. c_1.

From (1), therefore,

$$(6)\quad E = -\frac{RT}{nF}\log_e\frac{C}{c} + \frac{RT}{nF}\log_e\frac{C}{c_1} = \frac{RT}{nF}\log_e\frac{c}{c_1}.$$

or, at ordinary temperature, from (2)

$$E = \frac{0{\cdot}058}{n}\log\frac{c}{c_1}.$$

E.M.F. of Galvanic Element

The electromotive force of a galvanic element of the form

Metal M of valency n	solution of salt of metal M in which the conc. of the metal ions is c	solution of salt of metal M_1 in which the conc. of the metal ions is c_1	Metal M_1 of valency n_1

is, from (1) and (5),

$$(7)\quad E = \epsilon - \epsilon_1 = -\frac{RT}{nF}\log_e\frac{C}{c} + \frac{RT}{n_1F}\log_e\frac{C_1}{c_1} = \epsilon_o + \frac{RT}{nF}\log_e c - \epsilon_{o1} - \frac{RT}{n_1F}\log_e c_1.$$

ϵ and ϵ_1 are the potential differences between the metals M and M_1 and their respective solutions, and ϵ_o and ϵ_{o1} the normal potentials of the metals M and M_1.

Diffusion-potential

The diffusion-potential at the junction of two solutions of different concentrations of the same binary electrolyte, composed of two univalent ions, is

$$(8)\quad \epsilon = \frac{l_C - l_A}{l_C + l_A}\cdot\frac{RT}{F}\log_e\frac{c}{c_1}.$$

c is the concentration of the ions in the concentrated solution and c_1 that in the dilute solution. l_C and l_A are the ionic conductivities of the positive and negative ions respectively

(p. 104). The sign of ϵ is that of the potential of the dilute solution with respect to the concentrated solution. It should be noted that the potential of the dilute solution is of the same sign as the faster moving ion.

At the junction of two solutions of different binary electrolytes of the same ionic concentration, and when each electrolyte gives only univalent ions, the diffusion-potential is

$$(9)\quad \epsilon = \frac{RT}{F} \log_e \frac{l_C + l'_A}{l'_C + l_A},$$

where l_C and l_A are the ionic conductivities of the ions of the one electrolyte, and l'_C and l'_A those of the other.

Oxidation-reduction Potential

Every oxidation process in which ions take part can be regarded as a taking-up of positive charges or a giving-up of negative charges, and, conversely, every reduction as a giving-up of positive or a taking-up of negative charges. The oxidation of ferrous to ferric ions, for example, may be represented by the equation

$$\mathrm{Fe}^{\cdot\cdot} + \oplus = \mathrm{Fe}^{\cdot\cdot\cdot}.$$

If such a process takes place at an indifferent (unattackable) electrode, a potential-difference between the electrode and the solution is developed. The magnitude of this potential-difference depends on the concentrations of the substances taking part in the reaction. Thus for the reaction

$$\mathrm{mA} + \mathrm{nB} + nF = \mathrm{pC} + \mathrm{qD},$$

in which m molecules of A and n molecules of B are converted into p molecules of C and q molecules of D by taking up n faradays of positive electricity, the electrode-potential ϵ is given by the equation

$$(10)\quad \epsilon = \epsilon_0 + \frac{RT}{nF} \log_e \frac{[\mathrm{C}]^p\,[\mathrm{D}]^q}{[\mathrm{A}]^m\,[\mathrm{B}]^n}.$$

The square brackets denote the concentrations of the enclosed substances. ϵ_0 is the normal potential of the electrode reaction. It is the potential of the electrode against the solution when all the substances A, B, C and D, which determine the potential, are present in unit concentration. In the numerator of the logarithmic expression are the concentrations of those substances which are formed by the taking-up of positive charges (i.e. the higher state of oxidation).

Affinity of Reaction

The affinity of a chemical reaction (p. 67) which takes place reversibly in a galvanic element is

(11) $A = nFE$ volt-coulombs or joules,

where E is the electromotive force of the element in volts, $F = 96540$ coulombs, and n the number of faradays which flow through the cell during the transformation of the quantities of the reacting substances given by the chemical equation representing the cell-reaction. Thus for the reaction

$$2H_2 + O_2 = 2H_2O$$

$n = 4$, since 4 equivalents of hydrogen or of oxygen are transformed in the formation of 2 molecules of water and 1 faraday flows through the cell during the transformation of each equivalent.

Since 1 joule = 0·2387 calorie, we obtain from (11)

(12) $A = nFE \times 0{\cdot}2387$
$= nE \times 96540 \times 0{\cdot}2387$
$= nE \times 23040$ calories.

Gibbs-Helmholtz Equation

If A is the maximum work obtainable from a chemical reaction at absolute temperature T and Q is the heat evolved during the reaction (as measured in a calorimeter), then according to the Gibbs-Helmholtz equation,

$$(13)\quad A = Q + T\frac{dA}{dT}.$$

$\frac{dA}{dT}$ is the temperature-coefficient of the maximum work, or the amount by which A is altered for a temperature-change of 1°, and may be positive, negative or zero. A and Q should, of course, be expressed in the same unit of energy.

From (11) and (13) we obtain

$$(14)\quad E = \frac{Q}{nF} + T\frac{dE}{dT},$$

from which the electromotive force E of a galvanic element at T° absolute may be calculated from Q, the heat of the reaction taking place in the element, and the temperature-

coefficient of the electromotive force $\frac{dE}{dT}$. To express E in volts, Q must be expressed in volt-coulombs. If Q is given in calories, then, since 0·2387 calorie = 1 volt-coulomb,

$$(15)\ E = \frac{Q}{nF \times 0{\cdot}2387} + T\frac{dE}{dT} = \frac{Q}{n \times 96540 \times 0{\cdot}2387} + T\frac{dE}{dT}$$

$$= \frac{Q}{23040n} + T\frac{dE}{dT} \text{ volt.}$$

E.M.F.—Examples

PROBLEM 324.—The normal potential of Cd is $\epsilon_o = -0{\cdot}420$ volt and of Ag $\epsilon_{o1} = 0{\cdot}798$ volt, both referred to the N-H· electrode as zero. Neglecting the diffusion-potential at the junction of the two electrolytes, calculate the electromotive force E of the cell

$$\text{Cd} \mid c = 0{\cdot}5 \text{ mol. N-Cd}(NO_3)_2 \mid c_1 = 0{\cdot}1 \text{ N-AgNO}_3 \mid \text{Ag}$$

at 18°, given that the degree of dissociation of the $Cd(NO_3)_2$ solution is $\alpha = 0{\cdot}48$ and of the $AgNO_3$ solution $\alpha_1 = 0{\cdot}81$.

SOLUTION 324.—The concentration of the Cd··-ions in the $c = 0{\cdot}5$ mol. N-solution is $ac = 0{\cdot}48 \times 0{\cdot}5$ gram-ion per litre. The concentration of the Ag·-ions in the $c_1 = 0{\cdot}1$ N-$AgNO_3$ solution is $\alpha_1 c_1 = 0{\cdot}81 \times 0{\cdot}1$ gram-ion per litre. From (7), therefore,

$$E = \epsilon_o + \frac{RT}{nF}\log_e ac - \epsilon_{o1} - \frac{RT}{n_1 F}\log_e \alpha_1 c_1,$$

and, since n for Cd = 2 and n_1 for Ag = 1, we obtain at 18°

$$E = -0{\cdot}420 + 0{\cdot}029 \log (0{\cdot}48 \times 0{\cdot}5) - 0{\cdot}798 - 0{\cdot}058 \log (0{\cdot}81 \times 0{\cdot}1)$$

$$= -0{\cdot}420 + (0{\cdot}029 \times -0{\cdot}6198) - 0{\cdot}798 - (0{\cdot}058 \times -1{\cdot}091)$$

$$= -0{\cdot}420 - 0{\cdot}018 - 0{\cdot}798 + 0{\cdot}063$$

$$= -1{\cdot}173 \text{ volt.}$$

The Cd is, therefore, the negative pole, or, in the cell the current flows from the Cd to the Ag.

PROBLEM 325.—The electromotive force of the cell

$$\text{Hg} \left| \begin{matrix} Hg_2Cl_2 \text{ in} \\ \text{N-KCl} \end{matrix} \right| \begin{matrix} \text{HgO in} \\ \text{N-NaOH} \end{matrix} \left| \text{Hg} \right.$$

is 0·168 volt at 18°. The degree of dissociation of N-KCl and of N-NaOH is 0·72. The ionic conductivity of K· is $l_c = 64{\cdot}9$,

of Cl' $l_A = 65{\cdot}4$, of $Na\cdot$ $l'_C = 43{\cdot}6$ and of OH' $l'_A = 174$ at 18°. Taking the concentration of the $Hg\cdot\cdot$-ions in a saturated solution of Hg_2Cl_2 in N-KCl (normal calomel electrode) as $c = 3 \times 10^{-20}$ gram-ion per litre, calculate the solubility-product of $Hg(OH)_2$ at 18°.

SOLUTION 325.—According to (9) the diffusion-potential at the junction of the two electrolytes KCl and NaOH is

$$\epsilon = 0{\cdot}058 \log \frac{l_C + l'_A}{l'_C + l_A} = 0{\cdot}058 \log \frac{64{\cdot}9 + 174}{43{\cdot}6 + 65{\cdot}4}$$

$$= 0{\cdot}058 \log \frac{238{\cdot}9}{109{\cdot}0}$$

$$= 0{\cdot}0198 \text{ volt.}$$

Since OH' is by far the fastest moving ion the KCl solution will be negative with respect to the NaOH solution, and the diffusion-potential must, therefore, be subtracted from the total electromotive force of the cell to obtain the electromotive force of the Hg concentration-cell alone. The latter is, therefore,

$$E = 0{\cdot}168 - 0{\cdot}0198 = 0{\cdot}1482 \text{ volt.}$$

If c_1 is the concentration of the $Hg\cdot\cdot$-ions in the NaOH solution saturated with HgO, we obtain from (6), since $n = 2$,

$$E = \frac{0{\cdot}058}{2} \log \frac{c}{c_1} = 0{\cdot}029 \log \frac{3 \times 10^{-20}}{c_1},$$

$\therefore \log c_1 = \overline{26}{\cdot}684$ and $c_1 = 4{\cdot}83 \times 10^{-26}$ gram-ion per litre.

The solubility-product of $Hg(OH)_2$ is (p. 121)

$$L = [Hg\cdot\cdot]\,[OH']^2.$$

In N-NaOH saturated with HgO we have just found $[Hg\cdot\cdot] = c_1 = 4{\cdot}83 \times 10^{-26}$, and, since the degree of dissociation of the N-NaOH is 0·72, the concentration of the OH'-ions is $1 \times 0{\cdot}72$, or $[OH'] = 0{\cdot}72$. Therefore

$$L = (4{\cdot}83 \times 10^{-26})\,(0{\cdot}72)^2$$

$$= \mathbf{2{\cdot}5 \times 10^{-26}}.$$

PROBLEM 326.—The E.M.F. of the cell

$$Ag \mid c = 0{\cdot}01 \text{ N-}AgNO_3 \left| \begin{matrix} \text{saturated} \\ NH_4NO_3 \end{matrix} \right| c_1 = 0{\cdot}001 \text{ N-}AgNO_3 \mid Ag$$

is $E = 0{\cdot}0579$ volt at 25°. Assuming that the interposition of saturated NH_4NO_3 solution completely eliminates the

diffusion-potential, and that the 0·001 N-$AgNO_3$ solution is completely dissociated, calculate the degree of dissociation and the concentration of the $Ag^{\cdot}$-ions in the 0·01 N-$AgNO_3$ solution.

SOLUTION 326.—If a is the degree of dissociation of the $c = 0{\cdot}01$ N-solution, the concentration of the $Ag^{\cdot}$-ions is ac. Since the $c_1 = 0{\cdot}001$ N-solution is completely dissociated, the concentration of the $Ag^{\cdot}$-ions in it is c_1. For the E.M.F. of the Ag concentration-cell we therefore obtain from (6)

$$E = \frac{RT}{nF} \log_e \frac{ac}{c_1},$$

and, since $n = 1$, at 25°

$$0{\cdot}0579 = 0{\cdot}059 \log \frac{a \times 0{\cdot}01}{0{\cdot}001},$$

$$\therefore a = \mathbf{0{\cdot}958}.$$

The concentration of the $Ag^{\cdot}$-ions in the $c = 0{\cdot}01$ N-solution is

$$[Ag^{\cdot}] = ac = 0{\cdot}958 \times 0{\cdot}01 = \mathbf{0{\cdot}00958} \text{ gram-ion per litre.}$$

PROBLEM 327.—The normal potential of silver is $\epsilon_{Ag} = + 0{\cdot}771$ volt (hydrogen standard), that of chlorine at atmospheric pressure is $\epsilon_{Cl_2} = + 1{\cdot}366$ volt, and that of bromine at atmospheric pressure is $\epsilon_{Br_2} = + 0{\cdot}99$ volt. The solubility-product of AgCl at 25° is $L_1 = 2 \times 10^{-10}$, and that of AgBr $L_2 = 2 \times 10^{-13}$. What is the affinity of silver, in joules and calories, (*a*) to chlorine under atmospheric pressure, (*b*) to bromine-vapour under atmospheric pressure?

SOLUTION 327.—(*a*) The affinity of silver to chlorine at atmospheric pressure is defined as the maximum work which can be gained by the reversible combination of 1 molecule of chlorine at atmospheric pressure with 2 equivalents of metallic silver to form two molecules of solid silver chloride, according to the equation $Cl_2 + 2Ag = 2AgCl$.

This reaction proceeds reversibly, and therefore yields the maximum work, in a galvanic element of the type

$$Ag \;\Big|\; \text{saturated solution of AgCl} \;\Big|\; \text{Pt charged with } Cl_2 \text{ at atmospheric pressure.}$$

When the element is in action, Ag goes into solution as $Ag^{\cdot}$-ions at one electrode and Cl_2 as Cl'-ions at the other, and

solid AgCl is formed. If E denotes the E.M.F. of the element, then by the solution of 1 molecule of Cl_2 and 2 equivalents of Ag the electrical energy

$$A = 2E \times 96540 \text{ joules}$$

is produced. E can be calculated from the two separate electrode potentials, ϵ_1 between the silver electrode and the solution and ϵ_2 between the chlorine electrode and the solution.

From (1) and (3)

$$\epsilon_1 = + \frac{RT}{nF} \log_e \frac{[Ag^+]}{C_{Ag}} \text{ and } \epsilon_2 = + \frac{RT}{nF} \log_e \frac{C_{Cl_2}}{[Cl^-]}.$$

C_{Ag} and C_{Cl_2} are the concentrations of the Ag^+- and Cl^--ions corresponding to the electrolytic solution pressures of silver and of chlorine at atmospheric pressure. The square brackets, as usual, denote the concentrations of the ions at the electrodes. Since in both cases $n = 1$, we obtain from (7)

$$E = \epsilon_1 - \epsilon_2 = \frac{RT}{F} \log_e \frac{[Ag^+]}{C_{Ag}} - \frac{RT}{F} \log_e \frac{C_{Cl_2}}{[Cl^-]}$$

$$= \frac{RT}{F} \log_e [Ag^+][Cl^-] - \frac{RT}{F} \log_e C_{Ag} - \frac{RT}{F} \log_e C_{Cl_2}$$

$$= \frac{RT}{F} \log_e [Ag^+][Cl^-] + \epsilon_{Ag} - \epsilon_{Cl_2}.$$

The product $[Ag^+][Cl^-]$ is equal to the solubility-product L_1 of silver chloride, since the solution is saturated with AgCl. Therefore

$$E = \frac{RT}{F} \log_e L_1 + \epsilon_{Ag} - \epsilon_{Cl_2}$$

and, at 25°,

$$E = 0{\cdot}059 \log 2 \times 10^{-10} + 0{\cdot}771 - 1{\cdot}366$$
$$= 0{\cdot}059 \times -9{\cdot}699 - 0{\cdot}595 = -1{\cdot}167 \text{ volt.}$$

The negative sign means that the silver electrode, which in the calculation was taken as positive ($+\epsilon_1$), is the negative pole. In the calculation of A the sign of E is of no consequence; it is only the absolute value that is required.

The affinity of silver to chlorine at atmospheric pressure is, therefore,

$$A = 2 \times 1{\cdot}167 \times 96540 = \mathbf{225300} \text{ joules}$$

or, in heat units,

$$A = 2 \times 1{\cdot}167 \times 23040 = \mathbf{53760} \text{ calories.}$$

(*b*) For the affinity of silver to bromine-vapour at atmospheric pressure we have the corresponding equation

$$A = 2E \times 96540 \text{ joules,}$$

where E is the E.M.F. of the galvanic element

Ag	solution saturated with AgBr	Pt charged with Br-vapour at atmospheric pressure.

As above

$$E = \frac{RT}{F} \log_e L_2 + \epsilon_{Ag} - \epsilon_{Br_2}$$
$$= 0{\cdot}059 \log 2 \times 10^{-13} + 0{\cdot}771 - 0{\cdot}99$$
$$= 0{\cdot}969 \text{ volt,}$$

and

$$A = 2 \times 0{\cdot}969 \times 96540 = \mathbf{187100} \text{ joules.}$$
$$= 2 \times 0{\cdot}969 \times 23040 = \mathbf{44640} \text{ calories.}$$

PROBLEM 328.—The solubility of silver chloride in water at 25° C. is $S = 1{\cdot}4 \times 10^{-5}$ gram-molecules per litre. The solubility in ammonia solutions is greater, and is proportional to the total concentration of the ammonia. The factor of proportionality is $k = 0{\cdot}05$. The increased solubility in ammonia depends on the formation of a complex ion according to the scheme $Ag^{\cdot} + n NH_3 = Ag(NH_3)_n^{\cdot}$. How many molecules of ammonia take part in the formation of this complex cation, i.e. what is the value of n, and what is the dissociation-constant $K = \frac{[Ag^{\cdot}]\,[NH_3]^n}{[Ag(NH_3)_n^{\cdot}]}$ of the complex ion?

SOLUTION 328.—In any solution which is saturated with silver chloride the product of the concentrations of the ions, $[Ag^{\cdot}]\,[Cl']$, must, for a given temperature, have a definite constant value L, which is called the solubility-product of silver chloride. In a saturated aqueous solution which contains only silver chloride, $[Ag^{\cdot}] = [Cl'] = S$, and, therefore, $L = S^2$, if we assume that the dissociation of the dissolved salt is complete. The greater solubility of silver chloride in solutions of ammonia compared with pure water is caused by

the formation of a complex cation by the addition of ammonia to the $Ag^{\cdot}$-ions according to the scheme

$$Ag^{\cdot} + nNH_3 = Ag(NH_3)_n^{\cdot};$$

this diminishes the concentration of the silver ions, and, therefore, requires an increase in the concentration of the chlorine ions, so that the value of the solubility-product may be maintained. The application of the law of mass-action to the formation of the complex cation leads to the equilibrium-equation

$$(1)\quad \frac{[Ag^{\cdot}]\,[NH_3]^n}{[Ag(NH_3)_n^{\cdot}]} = K.$$

n must, of course, be a whole number.

The total concentration of silver in the solution, a, is equal to the sum of the concentrations of the $Ag^{\cdot}$-ions and the $Ag(NH_3)_n^{\cdot}$-ions, if we assume that the salts AgCl and the $Ag(NH_3)_nCl$ are practically completely dissociated. According to the conditions of the problem, the solubility of AgCl in the ammonia solution is

$$(2)\quad a = [Ag^{\cdot}] + [Ag(NH_3)_n^{\cdot}] = k(NH_3).$$

Here (NH_3) denotes the total concentration of ammonia in the solution, and, therefore,

$$(3)\quad (NH_3) = [NH_3] + [NH_4^{\cdot}] + n\,[Ag(NH_3)_n^{\cdot}],$$

since the total ammonia in the solution is equal to the sum of the undissociated ammonia, the ammonium ions and the ammonia in the complex ion. From (2) we therefore obtain

$$(4)\quad [Ag^{\cdot}] + [Ag(NH_3)_n^{\cdot}] = k[NH_3] + k[NH_4^{\cdot}] + kn[Ag(NH_3)_n^{\cdot}].$$

When the concentration of ammonia is sufficiently great, the concentration of the silver ions, $[Ag^{\cdot}]$, which is always less than $\mathfrak{S}$, that is, less than $1{\cdot}25 \times 10^{-5}$, may be neglected in comparison with the total concentration of silver a. Under these circumstances we obtain from (2)

$$a = [Ag(NH_3)_n^{\cdot}],$$

and hence from (4)

$$a = k[NH_3] + k[NH_4^{\cdot}] + kna,$$
$$a(1 - kn) = k\{[NH_3] + [NH_4^{\cdot}]\}$$

and

$$(5)\quad a = \frac{k}{1 - kn}\{[NH_3] + [NH_4^{\cdot}]\}.$$

By dividing the equation

$$[Ag\cdot]\,[Cl'] = L$$

by equation (1) written in the form

$$\frac{[Ag\cdot]\,[NH_3]^n}{a} = K,$$

we obtain

$$(6)\quad \frac{a[Cl']}{[NH_3]^n} = \frac{L}{K}.$$

Every molecule of AgCl which dissolves produces one $Ag(NH_3)_n\cdot$-ion and one Cl'-ion. The concentrations of these ions are, therefore, equal and $[Cl'] = a$, and (6) becomes

$$(a)^2 = \frac{L}{K}[NH_3]^n,$$

and, therefore,

$$(7)\quad a = \sqrt{\frac{L}{K}[NH_3]^n}.$$

When equations (5) and (7) are compared, it is evident, since $\frac{k}{1 - kn}$ and $\sqrt{\frac{L}{K}}$ are constants, that for different concentrations of ammonia the two equations can be simultaneously satisfied only (*1*) if the concentration of the ammonium ions, $[NH_4\cdot]$, is negligible compared with the concentration of the undissociated ammonia molecules, $[NH_3]$, a condition which is satisfied in the case of weak bases like ammonia, and (*2*) if $\mathbf{n = 2}$. From (5) and (7) we then obtain

$$a = \frac{k}{1 - 2k}[NH_3] = \sqrt{\frac{L}{K}}[NH_3],$$

$$\frac{k}{1 - 2k} = \sqrt{\frac{L}{K}},$$

and

$$\mathbf{K} = \frac{L(1 - 2k)^2}{k^2} = \frac{(1{\cdot}4)^2 \times 10^{-10} \times (0{\cdot}9)^2}{(0{\cdot}05)^2}$$

$$= 5{\cdot}4 \times 10^{-8}.$$

The silver-ammonia complex ion has, therefore, the composition $Ag(NH_3)_2\cdot$, and its dissociation-constant at 25° C. is $5{\cdot}4 \times 10^{-8}$.

PROBLEM 329 (cf. preceding problem).—What are the E.M.F.'s, E_1 and E_2 of the cells

$$\mathrm{Ag}/c\ \mathrm{N\text{-}AgNO_3}/c'\ \mathrm{N\text{-}KCl,\ AgCl/Ag}$$

and

$$\mathrm{Ag}\ \Big|\ \begin{matrix} c\ \mathrm{N\text{-}AgNO_3} \\ C\ \mathrm{N\text{-}NH_3} \end{matrix}\ \Big|\ c'\ \mathrm{N\text{-}KCl,\ AgCl}\ \Big|\ \mathrm{Ag}$$

if $c = 0{\cdot}01$, $c' = 1$ and $C = 1$?

SOLUTION 329.—According to Nernst's formula (equation (6)) the E.M.F. of a concentration cell is

$$E = \frac{RT}{nF} \log_e \frac{[\mathrm{Me}\cdot]_1}{[\mathrm{Me}\cdot]_2},$$

if the diffusion-potential at the point of contact of the two electrolytes, in which the electrodes are placed, is neglected. n is the valency of the cation, $[\mathrm{Me}\cdot]_1$ and $[\mathrm{Me}\cdot]_2$ the concentrations of the cation at the two electrodes. The cells described in the problem are to be regarded as concentration cells with respect to the $\mathrm{Ag}\cdot$ cation, and, since $n = 1$ in this case, the formula becomes

$$E = \frac{RT}{F} \log_e \frac{[\mathrm{Ag}\cdot]_1}{[\mathrm{Ag}\cdot]_2}.$$

The concentrations of the silver ions, $[\mathrm{Ag}\cdot]$, in the various solutions may be calculated as follows.

In the c N-$AgNO_3$ solution the silver ion concentration, $[\mathrm{Ag}\cdot]_1$, is approximately equal to the total concentration, since the salt may be regarded as practically completely dissociated,

$$\therefore [\mathrm{Ag}\cdot]_1 = c.$$

In c' N-KCl solution, which is saturated with AgCl, the product of the silver ion concentration, $[\mathrm{Ag}\cdot]_2$, and the chlorine ion concentration, $[\mathrm{Cl}']$, must be equal to L, the solubility-product of AgCl (cf. problem 328). If the KCl is regarded as completely dissociated, $[\mathrm{Cl}'] = c'$. We obtain, therefore,

$$[\mathrm{Ag}\cdot]_2\,[\mathrm{Cl}'] = L,$$

$$[\mathrm{Ag}\cdot]_2 = \frac{L}{[\mathrm{Cl}']} = \frac{L}{c'},$$

and, for the E.M.F. of the first cell at 25° C.,

$$\mathrm{E}_1 = \frac{RT}{F} \log_e \frac{cc'}{L},$$

$$= 0{\cdot}059 \log \frac{0{\cdot}01}{2 \times 10^{-10}} = \mathbf{0{\cdot}454}\ \text{volt.}$$

The concentration of the silver ions, $[Ag^{\cdot}]$, in the C N-ammonia solution follows from the equation (cf. problem 328)

$$(1)\quad \frac{[Ag^{\cdot}][NH_3]^2}{[Ag(NH_3)_2^{\cdot}]} = K.$$

Since K has a relatively small value ($5{\cdot}4 \times 10^{-8}$), the complex-formation between the silver ions and the excess of ammonia may be regarded as practically complete, i.e. practically the whole of the silver in the solution is present as the complex ion $Ag(NH_3)_2^{\cdot}$,

$$\therefore\ [Ag(NH_3)_2^{\cdot}] = c.$$

The concentration of the free ammonia is, therefore,

$$[NH_3] = C - 2c,$$

and, from equation (1), the concentration of the silver ions is

$$[Ag^{\cdot}] = \frac{Kc}{(C - 2c)^2}.$$

For E_2, the E.M.F. of the second cell, we therefore obtain

$$E_2 = \frac{RT}{F} \log_e \frac{Kc}{(C - 2c)^2} \times \frac{c'}{L},$$

$$= 0{\cdot}059 \log \frac{5{\cdot}4 \times 10^{-8} \times 0{\cdot}01 \times 1}{(0{\cdot}98)^2 \times 2 \times 10^{-10}} = 0{\cdot}059 \log 2{\cdot}8$$

$$= \mathbf{0{\cdot}0264}\ \text{volt.}$$

The addition of $C = 1$ N-ammonia to the 0·01 N-$AgNO_3$ solution has, therefore, diminished the E.M.F. by 0·454 − 0·0264 = 0·428 volt. The sign of the E.M.F., however, remains unchanged.

PROBLEM 330.—The E.M.F. of the hydrogen-oxygen cell at 25° is $E_1 = 1{\cdot}23$ volt, and the E.M.F. of the cell

$$Ag/\text{saturated solution of } Ag_2O/H_2$$

is $E_2 = 1{\cdot}18$ volt. What is the affinity of silver to oxygen under atmospheric pressure (a) at 25° and (b) at 35°, if the molecular heat of formation of Ag_2O is $Q = 6400$ cals.?

SOLUTION 330.—(a) The E.M.F. E of any galvanic element

which works reversibly is a measure of the affinity A of the reaction which produces the current; for

$$A = nE \times 96540 \text{ volt-coulombs},$$

if n denotes the number of equivalents of ions which enter, or are deposited from, the solution during the transformation of the quantities of the reacting substances given by the equation representing the cell-reaction. The E.M.F. of the hydrogen-oxygen cell

$$H_2/\text{any aqueous solution}/O_2$$

is, therefore, a measure of the affinity of the reaction

$$(1)\ 2H_2 + O_2 = 2H_2O,$$

and the E.M.F. of the cell

$$H_2/\text{saturated solution of } Ag_2O/Ag$$

is a measure of the affinity of the reaction

$$(2)\ H_2 + Ag_2O = H_2O + 2Ag.$$

By multiplying (2) by 2 and subtracting from (1) we obtain

$$(3)\ O_2 + 4Ag = 2Ag_2O,$$

or, for the affinities,

$$A_3 = A_1 - 2A_2.$$

Now

$$A_1 = 4E_1 \times 96540 \text{ volt-coulombs},$$

and $$A_2 = 2E_2 \times 96540 \text{ volt-coulombs},$$

$$\therefore A_3 = 4(E_1 - E_2)\ 96540 \text{ volt-coulombs},$$

$$= 0{\cdot}20 \times 96540 \text{ volt-coulombs},$$

$$= 0{\cdot}20 \times 23040 = 4608 \text{ calories at } 25^\circ \text{ C.}$$

(*b*) To calculate the affinity at 35° C. we use Helmholtz's equation (13)

$$A = Q + T\frac{dA}{dT} \text{ or } \frac{dA}{dT} = \frac{A - Q}{T}.$$

Q, the heat of formation of 2 molecules of Ag_2O, is 12800 calories, therefore

$$\left(\frac{dA}{dT}\right)_{T=298} = \frac{4608 - 12800}{298} = -27{\cdot}5 \text{ calories per degree.}$$

By raising the temperature 1° C. the affinity is diminished by 27·5 cals., and, therefore, for a rise of 10° C. by 275 cals.,

if the temperature-coefficient is assumed to be constant in the small interval between 25° and 35°. The affinity of silver to oxygen at 35° is, therefore,

$$4608 - 275 = 4333 \text{ cals.}$$

PROBLEM 331.—The potential of a mercury electrode in a $c = 1$ N-KCl solution which is saturated with calomel is $\epsilon_1 = +0{\cdot}283$ volt, and the solubility-product of calomel, Hg_2Cl_2, is $L = [Hg_2\cdot\cdot]\,[Cl']^2 = 3{\cdot}5 \times 10^{-18}$. When a $c' = 0{\cdot}001$ mol. N-$FeCl_3$ solution is shaken with solid calomel and metallic mercury, reduction of the ferric chloride proceeds until the ratio of ferric to ferrous ions in the solution becomes $[Fe\cdot\cdot\cdot]/[Fe\cdot\cdot] = x$. What is the value of x, if the normal oxidation-potential of a ferric-ferrous ion electrode is $\epsilon_0 = 0{\cdot}743$ volt?

SOLUTION 331.—Let the ratio of ferric to ferrous ions in the solution at equilibrium be x. Then the oxidation-potential of the solution is, from (10),

$$\epsilon = \epsilon_0 + \frac{RT}{F}\log_e x \text{ volt,}$$

since $n = 1$.

The mercury potential in the solution at equilibrium must have the same value, therefore

$$(1)\quad \epsilon_0 + \frac{RT}{F}\log_e x = \epsilon'_0 + \frac{RT}{2F}\log_e y,$$

where ϵ'_0 denotes the normal potential of mercury against mercurous ions, and y the concentration of the divalent ($n = 2$) mercurous ions, $[Hg_2\cdot\cdot]$, in the solution at equilibrium.

In equation (1) ϵ'_0, x and y are unknown, and therefore two further equations are necessary to enable us to calculate them. From the potential of the normal calomel electrode ϵ_1 we can obtain ϵ'_0 since

$$(2)\quad \epsilon_1 = \epsilon'_0 + \frac{RT}{2F}\log_e[Hg_2\cdot\cdot] = \epsilon'_0 + \frac{RT}{2F}\log_e\frac{L}{[Cl']^2} = \epsilon'_0 + \frac{RT}{2F}\log_e\frac{L}{c^2},$$

if the potassium chloride is regarded as completely dissociated.

y may be calculated from the extent to which the ferric chloride solution is reduced. The reduction takes place according to the equation

$$2\,Fe^{\cdot\cdot\cdot} + 2Hg = 2Fe^{\cdot\cdot} + Hg_2^{\cdot\cdot},$$
$$\text{or } 2FeCl_3 + 2Hg = 2FeCl_2 + Hg_2Cl_2.$$

For every 2 molecules of $FeCl_3$ reduced, 1 molecule of Hg_2Cl_2 is formed, and, since Hg_2Cl_2 is practically insoluble, it is deposited, and 2Cl′-ions disappear from the solution.

Now $[Fe^{\cdot\cdot\cdot}] + [Fe^{\cdot\cdot}] = c'$, the total concentration of iron in the solution,

$$\text{and } \frac{[Fe^{\cdot\cdot\cdot}]}{[Fe^{\cdot\cdot}]} = x, \text{ therefore } [Fe^{\cdot\cdot}] = \frac{c'}{1+x}.$$

In the original ferric chloride solution there were 3Cl′-ions for every $Fe^{\cdot\cdot\cdot}$-ion; the concentration of the Cl′-ions was, therefore, $3c'$. In the solution at equilibrium, for every $Fe^{\cdot\cdot\cdot}$-ion which has been reduced, or for every $Fe^{\cdot\cdot}$-ion which has been formed, 1Cl′-ion has disappeared from the solution. In the solution at equilibrium there remain, therefore,

$$3c' - \frac{c'}{1+x} = \frac{2c' + 3xc'}{1+x} \text{ Cl′-ions.}$$

Since the solution is saturated with Hg_2Cl_2, the equation

$$[Hg_2^{\cdot\cdot}]\,[Cl']^2 = L$$

must hold, and, therefore,

$$(3)\ [Hg_2^{\cdot\cdot}] = y = \frac{L}{[Cl']^2} = \frac{L(1+x)^2}{(c')^2(2+3x)^2}.$$

If in equation (1) we substitute the value of ϵ'_0 obtained in equation (2) and the value of y obtained in equation (3), we obtain

$$\epsilon_0 + \frac{RT}{F}\log_e x = \epsilon_1 - \frac{RT}{2F}\log_e \frac{L}{c^2} + \frac{RT}{2F}\log_e \frac{L(1+x)^2}{(c')^2(2+3x)^2},$$

or, collecting the logarithmic terms on one side and dividing throughout by RT/F,

$$\log_e \frac{\sqrt{L}(1+x)}{c'(2+3x)} - \log_e x - \log_e \frac{\sqrt{L}}{c} = \frac{\epsilon_0 - \epsilon_1}{RT/F},$$

$$\log_e \frac{\sqrt{L}(1+x)c}{c'(2+3x)x\sqrt{L}} = \frac{\epsilon_0 - \epsilon_1}{RT/F},$$

$$\frac{c}{c'} \times \frac{1+x}{x(2+3x)} = e^{\frac{\epsilon_0-\epsilon_1}{RT}F},$$

$$(4)\quad \frac{1+x}{x(2+3x)} = e^{\frac{\epsilon_0-\epsilon_1}{RT}F} \times \frac{c'}{c}.$$

$e = 2{\cdot}718$ is the base of the natural logarithms. The right-hand side of equation (4) contains only known quantities. If, for brevity, we call its value A, we obtain from (4)

$$1 + x = x(2+3x)A = 2Ax + 3Ax^2,$$

$$x^2 + \frac{2A-1}{3A}x = \frac{1}{3A},$$

$$\therefore x = -\frac{2A-1}{6A} + \sqrt{\left(\frac{2A-1}{6A}\right)^2 + \frac{1}{3A}}.$$

The value of A is obtained from the equation

$$A = e^{\frac{\epsilon_0-\epsilon_1}{RT}F} \times \frac{c'}{c} = (2{\cdot}718)^{\frac{0{\cdot}743-0{\cdot}283}{0{\cdot}059}} \times \frac{10^{-3}}{1}$$
$$= (2{\cdot}718)^{18} \times 10^{-3}$$
$$= 6{\cdot}56 \times 10^4.$$

Since A is very large, x must, according to equation (4), be very small. If in this equation we neglect the term in x^2 as small compared with x, we obtain approximately

$$x = \frac{1}{2A}.$$

The reduction of the ferric chloride to ferrous chloride is, therefore, practically complete.

PROBLEM 332.—With potassium iodide mercuric ions form the complex ion HgI_4''. The dissociation-constant of the complex ion is $K = \frac{[Hg^{\cdot\cdot}]\,[I']^4}{[HgI_4'']} = 5 \times 10^{-31}$. In presence of metallic mercury equilibrium between mercurous and mercuric ions is reached when $\frac{[Hg_2^{\cdot\cdot}]}{[Hg^{\cdot\cdot}]} = K_1 = 120$. (*1*) How many grams of mercurous iodide dissolve on shaking solid mercurous iodide with a litre of $c = 1$ N-potassium iodide solution, if the solubility of Hg_2I_2 is $a = 3{\cdot}1 \times 10^{-10}$ gram-molecule per litre? (*2*) What is the concentration of a KI

solution which dissolves equal weights (in grams) of Hg in the form of mercurous and mercuric salts?

SOLUTION 332.—(*1*) In any solution which is saturated with mercurous iodide the equation

$$[Hg_2^{\cdot\cdot}]\,[I']^2 = L$$

must be satisfied, where L is the solubility-product of Hg_2I_2. In a pure saturated aqueous solution of Hg_2I_2, in which the salt may be regarded as completely dissociated,

$$[Hg_2^{\cdot\cdot}] = a, \text{ and } [I'] = 2a,$$
$$(1)\ \therefore [Hg_2^{\cdot\cdot}][I']^2 = 4a^3 = L.$$

Mercurous ions react in presence of metallic mercury according to the equation $Hg_2^{\cdot\cdot} = Hg + Hg^{\cdot\cdot}$, until equilibrium is reached when

$$(2)\ \frac{[Hg_2^{\cdot\cdot}]}{[Hg^{\cdot\cdot}]} = K_1.$$

If the solution contains potassium iodide, the potassium iodide reacts with the mercuric ions to form the complex ion HgI_4'', according to the equation

$$Hg^{\cdot\cdot} + 4I' = HgI_4''.$$

The equilibrium equation for this reaction is, therefore,

$$(3)\ \frac{[Hg^{\cdot\cdot}]\,[I']^4}{[HgI_4'']} = K.$$

In the case of the potassium iodide solution which is saturated with mercurous iodide, equations (1), (2) and (3) must be simultaneously satisfied. In these equations $[Hg_2^{\cdot\cdot}]$, $[Hg^{\cdot\cdot}]$, $[HgI_4'']$ and $[I']$ are unknown. An additional equation is, therefore, required for their solution. This is obtained as follows from the initial concentration of KI, which is known. If the concentration of the undissociated molecules is neglected, i.e. if all the salts are regarded as completely dissociated, the total iodine in the solution is equal to the sum of the iodine present as I'- and HgI_4''-ions. Of the four iodine atoms contained in HgI_4'', only two are derived from the dissolved Hg_2I_2, and the other two from the KI originally present. The concentration of the free iodine ions is, therefore,

$$(4)\ [I'] = c - 2[HgI_4''].$$

By dividing (1) by (2) we obtain

$$(5)\ [\mathrm{Hg}\cdot\cdot][\mathrm{I}']^2 = \frac{L}{K_1},$$

and from (3) and (5)

$$(6)\ \frac{L}{K_1}[\mathrm{I}']^2 = K[\mathrm{HgI_4''}].$$

From (6) and (4) we obtain

$$(7)\ [\mathrm{HgI_4''}] = \frac{L}{KK_1}[\mathrm{I}']^2 = \frac{c - [\mathrm{I}']}{2}.$$

(7) is a quadratic equation containing only one unknown quantity [I'], which may, therefore, be calculated:

$$(8)\ [\mathrm{I}'] = -\frac{KK_1}{4L} + \sqrt{\frac{K^2K_1^2}{16L^2} + \frac{KK_1c}{2L}}.$$

According to (7)

$$[\mathrm{HgI_4''}] = \frac{c - [\mathrm{I}']}{2}.$$

If x grams of mercurous iodide dissolve, and if M is the molecular weight of Hg_2I_2, there are formed $\frac{2x}{M}$ equivalents of HgI_4'', if the concentrations of the $Hg_2\cdot\cdot$- and $Hg\cdot\cdot$-ions in the concentrated potassium iodide solution are neglected. From (7) we therefore obtain

$$(9)\ x = \frac{Mc - M[\mathrm{I}']}{4} \text{ grams.}$$

Substituting the numerical values in (8) we obtain

$$[\mathrm{I}'] = \frac{-5 \times 10^{-31} \times 120}{4 \times 4 \times (3{\cdot}1 \times 10^{-10})^3} + \sqrt{\frac{(5 \times 10^{-31} \times 120)^2}{16 \times 16 \times (3{\cdot}1 \times 10^{-10})^6} + \frac{5 \times 10^{-31} \times 120 \times 1}{2 \times 4 \times (3{\cdot}1 \times 10^{-10})^3}}$$
$$= -0{\cdot}126 + \sqrt{(0{\cdot}126)^2 + 0{\cdot}252}$$
$$= 0{\cdot}392,$$

and from (9)

$$x = \frac{554(1 - 0{\cdot}392)}{4} = \mathbf{84{\cdot}2} \text{ grams } Hg_2I_2.$$

(2) The ratio of mercurous to mercuric ions is always $K_1 = 120$. [Hg··], may, therefore, be neglected in compari-

son with $[Hg_2 \cdot \cdot]$, and the whole of the mercuric mercury may be regarded as contained in the complex ion. If, therefore, equal weights of mercury dissolve in the mercuric and mercurous forms, the weight of mercury in the mercuric complex HgI_4'' must be equal to that in the mercurous ions, or

$$(10)\ [HgI_4''] = \tfrac{1}{2}[Hg_2 \cdot \cdot].$$

From (3) and (10)

$$[Hg \cdot \cdot][I']^4 = \tfrac{1}{2}K[Hg_2 \cdot \cdot],$$

and from this equation and (2)

$$[I']^4 = \tfrac{1}{2}KK_1,$$

$$\therefore\ [I'] = \sqrt[4]{\frac{KK_1}{2}} = \sqrt[4]{\frac{5 \times 10^{-31} \times 120}{2}} = 7{\cdot}40 \times 10^{-8}.$$

From (10) and (1) we obtain

$$[Hg_2 \cdot \cdot] = 2\,[HgI_4''] = \frac{L}{[I']^2} = \frac{4 \times (3{\cdot}1)^3 \times 10^{-30}}{(7{\cdot}40)^2 \times 10^{-16}}$$

$$= 2{\cdot}18 \times 10^{-14},$$

and from (4)

$$c = [I'] + 2[HgI_4''] = 7{\cdot}40 \times 10^{-8} + 2{\cdot}18 \times 10^{-14}$$

$$= \mathbf{7{\cdot}40 \times 10^{-8}\ N.}$$

In all potassium iodide solutions of measurable concentration, therefore, the mercurous iodide dissolves chiefly as complex mercuric salt.

PROBLEM 333.—The normal potential of a copper electrode against cupric ions is $\epsilon_0 = +0{\cdot}329$ volt, the constant for the equilibrium between cupric and cuprous ions in presence of metallic copper is $[Cu \cdot]^2/[Cu \cdot \cdot] = K = 0{\cdot}6 \times 10^{-3}$ and the solubilities of cuprous chloride and bromide are $a = 1{\cdot}1 \times 10^{-3}$ and $b = 2{\cdot}04 \times 10^{-4}$ gram-molecules per litre respectively. What is the potential of a copper electrode (*1*) in a $c = 0{\cdot}1$ N - HCl solution which is saturated with cuprous chloride, and (*2*) in a $c = 0{\cdot}1$ N - HBr solution which is saturated with cuprous bromide? (*3*) What is the normal potential ϵ'_0 of a copper electrode against cuprous ions?

SOLUTION 333.—(*1*) and (*2*). In the solution which is saturated with CuCl, and which at the same time is in equilibrium with metallic copper, let the concentrations of the cupric $(Cu \cdot \cdot)$ and cuprous $(Cu \cdot)$ ions be x and x' respectively, and in the corresponding CuBr solution let the concentrations

of the cupric and cuprous ions be y and y' respectively. Then the potential of a copper electrode, regarded as a cupric electrode, against the CuCl solution is

$$(1)\quad \epsilon_1 = \epsilon_0 + \frac{RT}{2F}\log_e x,$$

and against the CuBr solution

$$(2)\quad \epsilon_2 = \epsilon_0 + \frac{RT}{2F}\log_e y.$$

x and y may be determined from the following considerations :—

1. The cupric and cuprous ions are in equilibrium with one another and with metallic copper according to the equation

$$Cu^{\cdot\cdot} + Cu = 2Cu^{\cdot},$$

therefore,

$$(3)\quad (x')^2 = Kx$$

and

$$(4)\quad (y')^2 = Ky.$$

2. The solutions are saturated with CuCl and CuBr respectively, therefore $[Cu^{\cdot}]\,[Cl'] = L_1$ and $[Cu^{\cdot}]\,[Br'] = L_2$, where L_1 and L_2 are the solubility-products of CuCl and CuBr. L_1 and L_2 are equal to the squares of the solubilities of CuCl and CuBr in water, if the salts are regarded as completely dissociated. According to the law of electroneutrality

$$[Cl'] = c + [Cu^{\cdot}] + 2[Cu^{\cdot\cdot}] = c + x' + 2x$$

and

$$[Br'] = c + [Cu^{\cdot}] + 2[Cu^{\cdot\cdot}] = c + y' + 2y,$$

therefore,

$$(5)\quad x'(c + x' + 2x) = a^2 = L_1,$$

and

$$(6)\quad y'(c + y' + 2y) = b^2 = L_2.$$

Equations (3) to (6) are sufficient for the evaluation of x, y, x' and y'.

From (3) $x = \frac{(x')^2}{K}$ and from (4) $y = \frac{(y')^2}{K}$. Putting these values of x and y into equations (5) and (6) we obtain

$$(7)\quad x'\left(c + x' + \frac{2(x')^2}{K}\right) = a^2$$

and

$$(8)\quad y'\left(c + y' + \frac{2(y'^{\,2})}{K}\right) = b^2.$$

Since, according to the conditions of the problem, x' is less than a and a is very small, $x' + \frac{2(x')^2}{K}$ may be neglected in comparison with c. Similarly $y' + \frac{2(y')^2}{K}$ may be neglected in comparison with c.

From (7) and (8) we therefore obtain

$$x' = \frac{a^2}{c} \text{ and } y' = \frac{b^2}{c},$$

and hence from (3) and (4)

$$x = \frac{a^4}{c^2K},\ y = \frac{b^4}{c^2K}.$$

Putting these values of x and y into equations (1) and (2) we obtain

$$\epsilon_1 = \epsilon_0 + \frac{RT}{2F}\log_e\frac{a^4}{c^2K} = \epsilon_0 + \frac{RT}{F}\log_e\frac{a^2}{c\sqrt{K}},$$

and

$$\epsilon_2 = \epsilon_0 + \frac{RT}{2F}\log_e\frac{b^4}{c^2K} = \epsilon_0 + \frac{RT}{F}\log_e\frac{b^2}{c\sqrt{K}},$$

and, substituting the numerical values,

$$\epsilon_1 = 0{\cdot}329 + 0{\cdot}059\log\frac{(1{\cdot}1\times10^{-3})^2}{0{\cdot}1\sqrt{0{\cdot}6\times10^{-3}}}$$
$$= 0{\cdot}329 + 0{\cdot}059\times -3{\cdot}31$$
$$= \mathbf{0{\cdot}134\ volt.}$$
$$\epsilon_2 = 0{\cdot}329 + 0{\cdot}059\log\frac{(2{\cdot}04\times10^{-4})^2}{0{\cdot}1\sqrt{0{\cdot}6\times10^{-3}}}$$
$$= 0{\cdot}329 + 0{\cdot}059\times -4{\cdot}77$$
$$= \mathbf{0{\cdot}047\ volt.}$$

(*3.*) The normal potential, ϵ'_0, of copper against a solution of cuprous ions is obtained as follows: the potential of a copper electrode against an x' N-solution of cuprous ions is

$$\epsilon_1 = \epsilon'_0 + \frac{RT}{F}\log_e x'.$$

In the solution saturated with cuprous chloride $\epsilon_1 = + 0{\cdot}134$ volt and $x' = \frac{a^2}{c}$, therefore,

$$\begin{aligned}\epsilon'_0 &= \epsilon_1 - \frac{RT}{F}\log_e x' \\ &= \epsilon_1 - \frac{RT}{F}\log_e \frac{a^2}{c} \\ &= 0{\cdot}134 - 0{\cdot}059 \log \frac{(1{\cdot}1 \times 10^{-3})^2}{0{\cdot}1} \\ &= 0{\cdot}134 + 0{\cdot}059 \times 4{\cdot}92 \\ &= \mathbf{0{\cdot}424\ volt.}\end{aligned}$$

PROBLEM 334.—The potential between the terminals of a lead accumulator, which is filled with 100 c.c. of molecular N-H_2SO_4, is $E = 1{\cdot}88$ volt at 25°. The normal potential of lead is $\epsilon_0 = - 0{\cdot}12$ volt, the normal oxidation-potential of a plumbic-plumbous ion electrode is $\epsilon'_0 = + 1{\cdot}80$ volt, and the solubility of lead sulphate is $a = 1{\cdot}26 \times 10^{-4}$ gram-molecule per litre. What is the concentration of plumbic ions at the lead peroxide electrode (*1*) when the accumulator is on open circuit, (*2*) after a discharge of 1 ampere-hour? (*3*) What is the potential between the terminals of the accumulator after this discharge?

SOLUTION 334.—(*1*) The chemical process which takes place during the discharge of the accumulator is

$$(1)\quad Pb + 2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$

or, written in ionic form,

$$(2)\quad Pb + Pb^{\cdot\cdot\cdot\cdot} = 2Pb^{\cdot\cdot}.$$

Lead peroxide, or rather its hydroxide, can be regarded as the hydroxide of tetravalent lead. In presence of lead peroxide as solid phase, and therefore at the positive electrode of the accumulator, the concentration of the tetravalent lead ions, $[Pb^{\cdot\cdot\cdot\cdot}]$, will be determined by the solubility of lead peroxide.

We may regard reaction (2) as made up of two reactions, one,

$$Pb \rightarrow Pb^{\cdot\cdot},$$

localised at the negative electrode, and the other,

$$Pb^{\cdot\cdot\cdot\cdot} \rightarrow Pb^{\cdot\cdot},$$

localised at the positive electrode. The potential difference

between the two electrodes must be equal to the difference of the single potential differences between the separate electrodes and the solution, therefore, from (5) and (10),

$$E = \epsilon_0 + \frac{RT}{2F}\log_e [\mathrm{Pb}\cdot\cdot] - \epsilon'_0 - \frac{RT}{2F}\log_e \frac{[\mathrm{Pb}\cdot\cdot\cdot\cdot]}{[\mathrm{Pb}\cdot\cdot]}.$$

$$(3) \quad = \epsilon_0 + \frac{RT}{F}\log_e [\mathrm{Pb}\cdot\cdot] - \epsilon'_0 - \frac{RT}{2F}\log_e [\mathrm{Pb}\cdot\cdot\cdot\cdot].$$

The lead peroxide electrode is here regarded as an oxidation electrode. E, ϵ_0 and ϵ'_0 are given; the required concentration of plumbic ions, $[\mathrm{Pb}\cdot\cdot\cdot\cdot]$, may, therefore, be determined, if $[\mathrm{Pb}\cdot\cdot]$ can be calculated. This can be done from the given solubility, a, of lead sulphate, with which the solution is saturated. In a saturated pure aqueous solution of lead sulphate, $[\mathrm{Pb}\cdot\cdot][\mathrm{SO_4}'']$ $= L = a^2$, if we assume that the dissociation is complete.*

In molecular N-$\mathrm{H_2SO_4}$ the concentration of the $\mathrm{SO_4}''$-ions would be $[\mathrm{SO_4}''] = 1$, if the dissociation of the acid were complete; if the degree of dissociation is assumed to be approximately 50 per cent., $[\mathrm{SO_4}''] = 0{\cdot}5$ and $[\mathrm{Pb}\cdot\cdot] = \frac{a^2}{0{\cdot}5}$. Therefore, from (3),

$$E = \epsilon_0 - \epsilon'_0 + \frac{RT}{F}\log_e \frac{a^2}{0{\cdot}5} - \frac{RT}{2F}\log_e [\mathrm{Pb}\cdot\cdot\cdot\cdot],$$

and, changing to common logarithms,

$$\log [\mathrm{Pb}\cdot\cdot\cdot\cdot] = \frac{2(\epsilon_0 - \epsilon'_0)}{2{\cdot}3RT/F} + 2\log \frac{a^2}{0{\cdot}5} - \frac{2E}{2{\cdot}3RT/F}$$

$$= -\frac{2 \times 1{\cdot}92}{0{\cdot}059} + 2\log 3{\cdot}17 \times 10^{-8} + \frac{2 \times 1{\cdot}88}{0{\cdot}059}.$$

The sign of E in the above equation must be taken as negative, because, according to (3), E is the potential difference between the lead electrode and the lead peroxide electrode, and as the lead electrode is the negative pole, $E = -1{\cdot}88$.

$$\log [\mathrm{Pb}\cdot\cdot\cdot\cdot] = \frac{-0{\cdot}08}{0{\cdot}059} - 2 \times 7{\cdot}5 = -16{\cdot}35$$

$$\therefore [\mathrm{Pb}\cdot\cdot\cdot\cdot] = 4{\cdot}5 \times 10^{-17} \text{ gram-ion per litre.}$$

(2) During the discharge the concentration of the sulphuric acid diminishes, and, according to reaction (1), to such an

* This assumption is, however, only approximately correct.

extent that for every equivalent of lead which goes into solution at the negative electrode one molecule of H_2SO_4 is deposited as $PbSO_4$. By a discharge of one ampere-hour, therefore, $\frac{3600}{96540} = 0{\cdot}037$ molecules of H_2SO_4 are so deposited and removed from the solution. The 100 c.c. of molecular N-H_2SO_4, which originally contained 0·1 molecule H_2SO_4, contain after the discharge only $0{\cdot}1 - 0{\cdot}037 = 0{\cdot}063$ molecules. The concentration of the H_2SO_4 is, therefore, only 0·63 molecular normal after the discharge. If we assume that the degree of dissociation of this acid is, approximately, 60 per cent., the concentration of the SO_4''-ions is

$$[SO_4''] = 0{\cdot}63 \times 0{\cdot}6 = 0{\cdot}38,$$

and the concentration of the $Pb\cdot\cdot$-ions $[Pb\cdot\cdot] = \frac{a^2}{0{\cdot}38}$.

The concentration of the $Pb\cdot\cdot\cdot\cdot$-ions also changes during the discharge with the change in concentration of the acid.

In the solution, which is saturated with lead peroxide, the equation

$$[Pb\cdot\cdot\cdot\cdot][OH']^4 = L_1$$

must always be satisfied, where L_1 denotes the solubility-product of plumbic hydroxide, and, since $[H\cdot][OH'] = K_1$, we obtain

$$[Pb\cdot\cdot\cdot\cdot] = \frac{L_1}{[OH']^4} = \frac{L_1[H\cdot]^4}{K_1^4} = K[H\cdot]^4.$$

In two solutions, which we may distinguish by the suffixes 1 and 2, we have, therefore,

$$\frac{[Pb\cdot\cdot\cdot\cdot]_1}{[Pb\cdot\cdot\cdot\cdot]_2} = \frac{[H\cdot]_1^4}{[H\cdot]_2^4}.$$

Before the discharge the $H\cdot$-ion concentration of the H_2SO_4 is $[H\cdot]_1 = 2 \times 0{\cdot}5 = 1$, if we assume the dissociation to take place only according to the equation $H_2SO_4 = 2H\cdot + SO_4''$; after the discharge it is $[H\cdot]_2 = 2 \times 0{\cdot}38 = 0{\cdot}76$. Therefore

$$[Pb\cdot\cdot\cdot\cdot]_2 = [Pb\cdot\cdot\cdot\cdot]_1 \times \frac{(0{\cdot}76)^4}{(1)^4}$$

$$= 4{\cdot}5 \times 10^{-17} \times 0{\cdot}33 = 1{\cdot}5 \times 10^{-17} \text{ gram-ion per litre.}$$

(*3*) The E.M.F. of the accumulator after the discharge follows from the equation (cf. (3))

$$-E = \epsilon_0 + \frac{RT}{2F}\log_e[\mathrm{Pb}\cdot\cdot] - \epsilon'_0 - \frac{RT}{2F}\log_e\frac{[\mathrm{Pb}\cdot\cdot\cdot\cdot]}{[\mathrm{Pb}\cdot\cdot]}$$

$$E = \epsilon'_0 - \epsilon_0 + \frac{RT}{2F}\log_e[\mathrm{Pb}\cdot\cdot\cdot\cdot] - \frac{RT}{F}\log_e[\mathrm{Pb}\cdot\cdot]$$

$$= 1{\cdot}80 + 0{\cdot}12 + 0{\cdot}0295\log 1{\cdot}5\times10^{-17} - 0{\cdot}059\log\frac{1{\cdot}58\times10^{-8}}{0{\cdot}38}$$

$$= 1{\cdot}92 - 0{\cdot}496 + 0{\cdot}436$$

$$= \mathbf{1{\cdot}86}\ \text{volt.}$$

E.M.F.—Problems for Solution

PROBLEM 335.—The equivalent conductivity at 18° of a 0·02 equivalent N-$ZnCl_2$ solution is 94 r.o., and the equivalent conductivity of $ZnCl_2$ at infinite dilution is 112 r.o. The normal potential of Zn (referred to the N-H· electrode as zero) is − 0·770 volt. What is the potential of Zn against a 0·02 equivalent N-$ZnCl_2$ solution at 18°?

Ans. − 0·830 volt.

PROBLEM 336.—At 25° the E.M.F. of the cell

$$\mathrm{Zn}/0{\cdot}5\ \text{mol. N-}ZnSO_4/0{\cdot}05\ \text{mol. N-}ZnSO_4/\mathrm{Zn}$$

is 0·018 volt. Neglecting the diffusion-potential at the junction of the electrolytes, and assuming the dilute solution to be 35 per cent. dissociated, calculate the degree of dissociation of the concentrated solution.

Ans. 0·142.

PROBLEM 337.—The E.M.F. of the cell

$$\mathrm{Ag}/0{\cdot}1\ \text{N-}AgNO_3/\text{saturated }NH_4NO_3/0{\cdot}01\ \text{N-}AgNO_3/\mathrm{Ag}$$

is 0·0556 volt at 25°. At 25° the specific conductivity of 0·1 N-$AgNO_3$ is $109{\cdot}3\times10^{-4}$ r.o., and of 0·01 N-$AgNO_3$ $12{\cdot}53\times10^{-4}$ r.o. On the assumption that the conductivity is a true measure of the ionic concentration, calculate the E.M.F. of the Ag concentration-cell given above, and compare with the value found.

Ans. Calculated value = 0·0555 volt.

PROBLEM 338.—The E.M.F. of a Daniell cell in which the Cu··- and Zn··-ion concentrations are equal is 1·1 volt at 18°. What is the E.M.F. at 18° of a Daniell cell in which

the $Cu^{\cdot\cdot}$-ion concentration is 0·0005 and the $Zn^{\cdot\cdot}$-ion concentration is 0·5 gram-ion per litre?

Ans. 1·013 volt.

PROBLEM 339.—At 25° the E.M.F. of the cell

$$Pb \mid 0.01 \text{ mol. } N\text{-}Pb(NO_3)_2 \mid \begin{matrix}\text{saturated} \\ NH_4NO_3\end{matrix} \mid \begin{matrix}\text{N-calomel} \\ \text{electrode}\end{matrix}$$

is − 0·469 volt, and that of the cell

$$Pb \mid 0.01 \text{ mol. } N\text{-}Pb(ClO_3)_2 \mid \begin{matrix}\text{saturated} \\ NH_4NO_3\end{matrix} \mid \begin{matrix}\text{N-calomel} \\ \text{electrode}\end{matrix}$$

is − 0·463 volt. The NH_4NO_3 solution eliminates the diffusion-potentials. If the $Pb(ClO_3)_2$ is assumed to be completely dissociated, what is the degree of dissociation of the $Pb(NO_3)_2$?

Ans. 62·1 per cent.

PROBLEM 340.—The E.M.F. of the cell

$$Pb \mid 0.01 \text{ mol. } N\text{-}Pb(NO_3)_2 \mid \begin{matrix}\text{saturated} \\ NH_4NO_3\end{matrix} \mid \begin{matrix}\text{N-calomel} \\ \text{electrode}\end{matrix}$$

is − 0·469 volt at 25°. The $Pb(NO_3)_2$ is 62 per cent. dissociated. What is the normal potential of Pb referred to the N-calomel electrode as zero?

Ans. − 0·405 volt.

PROBLEM 341.—At 25° the E.M.F. of the cell

$$Ag \mid 0.1 \text{ N-}AgNO_3 \mid \begin{matrix}\text{saturated} \\ NH_4NO_3\end{matrix} \mid 0.1 \text{ N-calomel electrode}$$

is 0·396 volt, and that of the cell

$$Ag \mid \begin{matrix}\text{saturated solution} \\ \text{of } Ag(C_2H_3O_2)\end{matrix} \mid \begin{matrix}\text{saturated} \\ NH_4NO_3\end{matrix} \mid \begin{matrix}\text{0·1 N-calomel} \\ \text{electrode}\end{matrix}$$

is 0·383 volt. 0·1 N-$AgNO_3$ is 82 per cent. dissociated. Calculate (*a*) the $Ag^{\cdot}$-ion concentration in the saturated solution of silver acetate and (*b*) the degree of dissociation of the saturated solution, given that the solubility of the silver acetate at 25° is 0·0664 gram-molecule per litre.

Ans. (*a*) 0·04938 gram-ion per litre, (*b*) 0·7435.

PROBLEM 342.—The E.M.F. of the cell

Ag/AgCNS in 0·1 N-KCNS/AgBr in 0·1 N-KBr/Ag

is 0·015 volt at 25°. The solubility of AgBr in pure aqueous solution is $7·2 \times 10^{-7}$ gram-molecule per litre. Neglecting the diffusion-potential and assuming that all the salts are completely dissociated, calculate (*a*) the solubility-product and (*b*) the solubility of AgCNS at 25°.

Ans. (*a*) $0·93 \times 10^{-12}$, (*b*) $0·96 \times 10^{-6}$ gram-molecule per litre.

PROBLEM 343.—The E.M.F. of the cell

$$\mathrm{Ag} \left| \begin{matrix} \mathrm{Ag_2C_2O_4 \text{ in}} \\ \text{0·01 mol. N-}\mathrm{K_2C_2O_4} \end{matrix} \right| \text{0·1 N-}\mathrm{AgNO_3} \left| \mathrm{Ag} \right.$$

is − 0·198 volt at 25°. Neglecting the diffusion-potential, and taking the 0·1 N-$AgNO_3$ as 83 per cent. dissociated and the 0·01 N-$K_2C_2O_4$ as completely dissociated, calculate (*a*) the solubility-product and (*b*) the solubility of silver oxalate.

Ans. (*a*) $1·3 \times 10^{-11}$, (*b*) $1·48 \times 10^{-4}$ gram-molecule per litre.

PROBLEM 344.—What is the E.M.F. at 25° of the cell

$$\mathrm{H_2/0·5\ N\text{-}HCl/0·1\ N\text{-}NaOH/H_2}$$

if the H_2 at each electrode is under atmospheric pressure and if the diffusion-potential is neglected? The degree of dissociation of 0·5 N-HCl = 0·87, of 0·1 N-NaOH = 0·9 and the ionic-product of water is $1·2 \times 10^{-14}$.

Ans. 0·738 volt.

PROBLEM 345.—What is the E.M.F. at 25° of the cell

$$\mathrm{H_2/0·5\ N\text{-}formic\ acid/1\ N\text{-}acetic\ acid/H_2}$$

if the diffusion-potential is neglected? The dissociation-constant of formic acid is 127×10^{-5} and of acetic acid $1·8 \times 10^{-5}$.

Ans. 0·0451 volt.

PROBLEM 346.—The E.M.F. of the cell

$$\mathrm{Ag} \left| \begin{matrix} \mathrm{AgCl \text{ in}} \\ \text{0·1 N-KCl} \end{matrix} \right| \begin{matrix} \text{saturated} \\ \mathrm{NH_4NO_3} \end{matrix} \left| \text{0·1 N-}\mathrm{AgNO_3} \right| \mathrm{Ag}$$

is − 0·450 volt at 25°. 0·1 N-KCl is 85 per cent. dissociated and 0·1 N-$AgNO_3$ 82 per cent. Calculate (*a*) the solubility-product and (*b*) the solubility of AgCl.

Ans. (*a*) $1{\cdot}65 \times 10^{-10}$, (*b*) $1{\cdot}28 \times 10^{-5}$ gram-molecule per litre.

PROBLEM 347.—The E.M.F. of the cell

$$Cu/CuSO_4 + 100\,H_2O/ZnSO_4 + 100\,H_2O/Zn$$

is 1·0960 volt at 0° C. and 1·0961 volt at 3° C. What is the heat of the reaction taking place in the cell?

Ans. 63390 cals.

PROBLEM 348.—The E.M.F. of the combination

$$Cl_2/\text{molten } PbCl_2/Pb$$

is given by the formula

$$E = 1{\cdot}263 - [0{\cdot}000679\ (t - 498)] \text{ volts},$$

where t is the temperature C. Calculate the heat of formation of lead chloride at 498° C.

Ans. 82500 cals.

PROBLEM 349.—At 18° the potential of a Cu electrode against a 0·005 mol. N-$Cu(NO_3)_2$ solution is 0·266 volt, referred to the N-H· electrode as zero. Assuming that the $Cu(NO_3)_2$ solution is completely dissociated, calculate the normal potential of Cu against Cu· ·-ions.

Ans. 0·333 volt.

PROBLEM 350.—The normal potential of Zn referred to the N-H· electrode as zero is − 0·770 volt and of Cu 0·329 volt. When excess of Zn is added to a solution of $CuSO_4$ the Zn displaces the Cu till equilibrium is reached. What is the ratio of the concentration of the Zn· ·- to the Cu· ·-ions at equilibrium? (At equilibrium the potentials of the Zn and Cu against the solution are equal.)

Ans. $[Zn\cdot\cdot]/[Cu\cdot\cdot] = 7{\cdot}94 \times 10^{37}$.

PROBLEM 351.—The normal potential of Ag referred to the N-calomel electrode as zero is 0·488 volt at 18°. Taking the absolute potential of the calomel electrode as 0·56 volt (Hg positive), calculate the electrolytic solution pressure of Ag in atmospheres.

Ans. $2{\cdot}04 \times 10^{-17}$.

PROBLEM 352.—When metallic copper is shaken with a solution of a cupric salt in absence of air at 20°, the reaction

$Cu + Cu^{\cdot\cdot} = 2\,Cu^{\cdot}$ proceeds till equilibrium is established. The concentrations of the $Cu^{\cdot\cdot}$- and $Cu^{\cdot}$-ions are then such that $[Cu^{\cdot}]/[Cu^{\cdot}]^2 = 2{\cdot}02 \times 10^4$. If the normal potential of Cu against $Cu^{\cdot\cdot}$-ions is 0·329 volt (hydrogen standard), what is the normal potential of Cu against $Cu^{\cdot}$-ions?

Ans. 0·454 volt.

PROBLEM 353.—When CuCl is dissolved in KCl solutions a complex salt of the formula $(KCl)_n{\cdot}(CuCl)_m$ is formed, which dissociates giving the ions $K^{\cdot}$ and $Cu_mCl'_{m+n}$. Two very dilute solutions of CuCl in 0·1 N-KCl were prepared, the one containing 4 times as much CuCl as the other. The E.M.F. of the cell

$$Cu \;\Big|\; \begin{matrix}\text{dilute solution of}\\ \text{CuCl in KCl}\end{matrix} \;\Big|\; \begin{matrix}\text{conc. solution of}\\ \text{CuCl in KCl}\end{matrix} \;\Big|\; Cu$$

was 0·0351 volt at 18°. On the assumption that practically the whole of the dissolved CuCl is present as complex salt, and that, on account of the very large excess of KCl over CuCl, the Cl'-ion concentration in the two solutions is the same, and that the dissociation of the KCl and of the com plex salt is complete, calculate the value of m.

Ans. 0·995 (∴ 1, as it must be a whole number).

PROBLEM 354 (cf. preceding problem).—Two solutions of KCl, one 0·21 N and the other 0·1 N, and each containing 0·0002 gram-molecule CuCl per litre, were prepared. The E.M.F. of the cell

Cu/dilute KCl solution/conc. KCl solution/Cu

was 0·0374 volt at 18°. Taking the value of m found above and on the assumptions made in the preceding problem, calculate the value of n.

Ans. $\dfrac{m+n}{m} = 2$, ∴ $n = 1$.

PROBLEM 355.—What is the total E.M.F at 18° of the cel

$$H_2/0{\cdot}1\text{ N-HCl}/0{\cdot}001\text{ N-HCl}/H_2$$

if the H_2 at each electrode is at atmospheric pressure? The 0·1 N-HCl is 92 per cent. dissociated and the 0·001 N-HCl is completely dissociated. The ionic conductivity of $H^{\cdot}$ is 318 and of Cl' 65·4.

Ans. 0·039 volt,

PROBLEM 356.—A saturated solution of $AgNO_2$ contains 0·0265 gram-molecule per litre at 25°. The E.M.F. of the cell

$$Ag \left| \begin{array}{c} AgNO_2 \text{ solution containing} \\ 0{\cdot}0224 \text{ gram-ion } Ag^{\cdot} \text{ per litre} \end{array} \right| \begin{array}{c} \text{saturated solution} \\ \text{of } AgNO_2 \end{array} \Big| Ag$$

is 0·011 volt at 25°. Calculate (*a*) the solubility-product of $AgNO_2$, (*b*) the degree of dissociation of the saturated solution.

Ans. (*a*) $2{\cdot}13 \times 10^{-4}$, (*b*) 0·551.

PROBLEM 357.—When $AgNO_2$ is dissolved in KNO_2 solutions the complex anion $Ag_m(NO'_2)_n$ is formed. The E.M.F. at 25° of the cell

$$Ag \left| \begin{array}{c} 0{\cdot}584 \text{ N-}KNO_2 \\ 0{\cdot}05 \text{ N-}AgNO_2 \end{array} \right| \begin{array}{c} 0{\cdot}584 \text{ N-}KNO_2 \\ 0{\cdot}025 \text{ N-}AgNO_2 \end{array} \Big| Ag$$

is 0·0170 volt, and of the cell

$$Ag \left| \begin{array}{c} 0{\cdot}379 \text{ N-}KNO_2 \\ 0{\cdot}025 \text{ N-}AgNO_2 \end{array} \right| \begin{array}{c} 0{\cdot}219 \text{ N-}KNO_2 \\ 0{\cdot}025 \text{ N-}AgNO_2 \end{array} \Big| Ag$$

is − 0·0295 volt. Assuming that practically the whole of the dissolved $AgNO_2$ exists as complex ion, and that the NO'_2-ion concentrations are proportional to the KNO_2 concentrations, calculate the values of m and n and hence the formula of the complex ion.

Ans. $m = 1{\cdot}04 (\therefore 1)$, $\frac{n}{m} = 2{\cdot}1$, $\therefore n = 2$ and formula of complex ion is $Ag(NO_2)_2$.

PROBLEM 358.—What is the diffusion-potential at 18° at the junctions

(*a*) 0·001 N-HCl/0·001 N-KCl and
(*b*) 0·001 N-KCl/0·001 N-KOH,

if all the electrolytes are assumed to be completely dissociated? The ionic conductivities of $H^{\cdot}$, $K^{\cdot}$, Cl' and OH' are 318, 64·9, 65·4 and 174 respectively at 18°.

Ans. (*a*) 0·0272 volt (HCl negative), (*b*) 0·0153 volt (KCl negative).

PROBLEM 359 (cf. preceding problem).—What is the total E.M.F. at 18° of the cell

$$H_2/0{\cdot}001\ N\text{-}HCl/0{\cdot}001\ N\text{-}KCl/0{\cdot}001\ N\text{-}KOH/H_2$$

if the H_2 at each electrode is under atmospheric pressure and all the electrolytes are completely dissociated? The ionic product of water is $1{\cdot}2 \times 10^{-14}$.

Ans. 0·4199 volt.

PROBLEM 360.—The E.M.F. of the cell

$$Cu/N\text{-}CuSO_4/N\text{-}ZnSO_4/Zn$$

is 1·1 volt at 18°. What is the maximum work (*a*) in joules, (*b*) in calories obtainable at 18° by the reversible displacement of Cu by Zn according to the equation

$$CuSO_4 + Zn = ZnSO_4 + Cu?$$

Ans. (*a*) 212300, (*b*) 50670.

PROBLEM 361.—The E.M.F. at 25° of the cell

Pt	0·0337 mol. N-$Tl(NO_3)_3$ 0·0216 mol. N-$TlNO_3$ 0·42 N-HNO_3	N-H·	H_2 at atmos. pr.

is 1·2008 volt. Taking the potential of H_2/N-H· as zero, calculate the normal potential of the thallic-thallous ion electrode. Assume that the concentrations of Tl···- and Tl·-ions are proportional to the concentrations of the corresponding nitrates and neglect the diffusion-potential. The HNO_3 is added to prevent hydrolysis of the $Tl(NO_3)_3$.

Ans. 1·195 volt.

PROBLEM 362 (cf. preceding problem).—What is the ratio of [Tl···] to [Tl·] at which the potential of a thallic-thallous ion electrode is zero (referred to the normal hydrogen electrode as standard)?

Ans. $[Tl\cdots]/[Tl\cdot] = 6{\cdot}1 \times 10^{-42}$.

CHAPTER XI

DIFFUSION—RADIOACTIVITY

Diffusion

WHEN a dissolved substance diffuses from a place of higher concentration c to a place of lower concentration $c - dc$, the amount which diffuses in unit time through unit cross-section is proportional to the concentration-gradient $\frac{dc}{dx}$, and is, therefore, equal to $D\frac{dc}{dx}$, (Fick's law), where dx is the thickness of the diffusion-layer. The factor of proportionality D is called the diffusion-coefficient of the dissolved substance.

Diffusion—Examples

PROBLEM 363.—An electrolytic trough contains a small rotating platinum cathode and a large platinum anode. The electrolyte is sulphuric acid which contains 0·0005 gram of iodine per c.c. At all potentials between 0·2 and 1·0 volt a constant current (residual current) of $C = 0{\cdot}001$ ampere passes through the cell. What is the thickness δ of the layer which clings by adhesion to the rotating cathode, if the area of the cathode surface is $A = 0{\cdot}2$ sq. cm. and the diffusion-coefficient of iodine is $D = 0{\cdot}6$ cm.^{2} per day? What is the value of the residual current if the sulphuric acid contains 0·0008 gram of iodine per c.c.?

SOLUTION 363.—Every electrolyte is decomposed by the passage of the electric current. For every electrolyte, however, a definite minimum E.M.F. is necessary for the free separation of the decomposition products at the electrodes. This minimum E.M.F. is called the decomposition-potential of the electrolyte. If the E.M.F. applied is less than the decomposition-potential, a current can pass only if the de-

composition - products at the electrodes are continuously removed by inter-action with some substance present in the solution. In the present case, for example, the hydrogen evolved at the cathode is "depolarised" by the iodine in the solution with formation of hydrogen iodide. The velocity with which this reaction takes place determines the strength of the current which flows through the electrolyte when an E.M.F. less than the decomposition - potential is applied. According to Nernst's theory, the velocity of the chemical reaction between iodine and hydrogen at the electrode is very great, whilst the diffusion of the iodine in the solution, by which the supply of iodine at the electrode is maintained, takes place slowly. The effective velocity of the depolarising reaction is, therefore, determined by the velocity of diffusion of the iodine to the electrode.

When the electrode of area A is rotated, a layer of solution is formed, which clings to the surface of the electrode in consequence of adhesion and rotates with it. The concentration of the iodine in this layer diminishes regularly from the value c (grams per c.c.), the concentration of the iodine in the rest of the solution, to the value 0 at the electrode. The thickness of this adhesion layer depends on the velocity of rotation. If δ is the thickness of the layer for a definite velocity of rotation, then, according to Fick's law, there diffuses to the electrode in the time dt the quantity of iodine $DA\frac{(c-0)}{\delta}dt$ grams, where D denotes the diffusion-coefficient of iodine. If M is the equivalent weight of iodine, the number of equivalents of hydrogen depolarised by the diffused iodine is $\frac{DAc}{\delta M}dt$. In the time dt the current C liberates the quantity of hydrogen $C \cdot \epsilon \cdot dt$, where ϵ denotes the quantity liberated by unit current in unit time, that is, by unit quantity of electricity. In the stationary condition, therefore,

$$C \cdot \epsilon \cdot dt = \frac{DAc}{\delta M}dt,$$

or the required thickness

$$\delta = \frac{DAc}{MC\epsilon}.$$

If C is given in amperes and if ϵ denotes the number of equivalents of hydrogen liberated by one ampere in one

second, that is, by one coulomb of electricity, then D must be expressed in cm.^{2}/second.

In the present example

$$D = \frac{0{\cdot}6}{86400} = 7{\cdot}0 \times 10^{-6}\text{cm.}^2\text{/sec.}, A = 0{\cdot}2 \text{ sq. cm.}, c = 0{\cdot}0005$$

gm. per c.c., $C = 0{\cdot}001$ amp., $M = 127$, $\epsilon = \frac{1}{96540}$ equiv.,

$$\therefore \delta = \frac{7{\cdot}0 \times 10^{-6} \times 0{\cdot}2 \times 0{\cdot}0005 \times 96540}{127 \times 0{\cdot}001} \text{ cm.}$$

$$= \mathbf{5{\cdot}3 \times 10^{-4}} \text{ cm.}$$

If the concentration of iodine in the solution is c' instead of c, then, if C' is the residual current in this case,

$$C' \cdot \epsilon \cdot dt = \frac{DAc'}{\delta M} dt,$$

and

$$C' = \frac{DAc'}{\epsilon \delta M}$$

$$= \frac{7{\cdot}0 \times 10^{-6} \times 0{\cdot}2 \times 0{\cdot}0008 \times 96540}{5{\cdot}3 \times 10^{-4} \times 127}$$

$$= \mathbf{0{\cdot}0016} \text{ amp.}$$

PROBLEM 364 (cf. preceding problem).—If the residual current in the preceding problem is $C = 0{\cdot}05$ ampere when, instead of iodine, the sulphuric acid contains 0·01 gram of bromine per c.c., what is the diffusion-coefficient of bromine?

SOLUTION 364.—If, instead of iodine, the solution contains bromine of concentration $c = 0{\cdot}01$, and if the residual current is $C = 0{\cdot}05$ ampere, the equation

$$C\epsilon = \frac{DAc}{\delta M}$$

applies in this case too, if D is the diffusion-coefficient and M the equivalent weight of bromine. We obtain, therefore,

$$D = \frac{C\epsilon\delta M}{Ac} = \frac{0{\cdot}05 \times 5{\cdot}3 \times 10^{-4} \times 80}{0{\cdot}2 \times 0{\cdot}01 \times 96540}$$

$$= 1{\cdot}1 \times 10^{-5} \text{ cm.}^2\text{/second,}$$

$$\therefore \mathbf{D} = \mathbf{0{\cdot}95} \text{ cm.}^2\text{/day.}$$

Radioactivity

A radioactive substance gradually loses its activity C according to the law (Rutherford)

$$C = C_0 e^{-\lambda t},$$

or

$$\log_e C = \log_e C_0 - \lambda t.$$

C_0 is the initial activity, C the activity after time t, e the base of the natural logarithms and λ a constant for the particular substance.

Radioactivity—Example

PROBLEM 365.—In a space filled with radium emanation the current strength under the influence of a strong potential difference, which is sufficient to produce a saturation current, is, at a definite point of time, $C_0 = 35{\cdot}4$ (in arbitrary units). After $t_1 = 12$ hours the current strength has diminished to $C_1 = 32{\cdot}4$, and after $t_2 = 200$ hours to $C_2 = 8{\cdot}10$. After what time has the current strength the value $C_3 = 10$, and after what time has it sunk to half its original value?

SOLUTION 365.—The current strength at any time is proportional to the amount of radium emanation present at that time. The decomposition of the radium emanation follows the exponential law

$$C = C_0 e^{-\lambda t}.$$

Taking logarithms of both sides we obtain

$$\log C = \log C_0 - \frac{\lambda t}{2{\cdot}3}.$$

The value of λ may be obtained from each of the equations

$$\log C_1 = \log C_0 - \frac{\lambda t_1}{2{\cdot}3}.$$

and

$$\log C_2 = \log C_0 - \frac{\lambda t_2}{2{\cdot}3}.$$

From the former we obtain

$$\lambda = \frac{2{\cdot}3 \log \frac{C_0}{C_1}}{t_1} = \frac{2{\cdot}3 \log \frac{35{\cdot}4}{32{\cdot}4}}{12} = \frac{2{\cdot}3 \times 0{\cdot}0385}{12} = 0{\cdot}00738,$$

and from the latter

$$\gamma = \frac{2{\cdot}3 \log \frac{C_0}{C_2}}{t_2} = \frac{2{\cdot}3 \log \frac{35{\cdot}4}{8{\cdot}10}}{200} = \frac{2{\cdot}3 \times 0{\cdot}641}{200} = 0{\cdot}00737.$$

The mean value of λ is, therefore, 0·00738.

The time, t_3, after which the current strength has the value $C_2 = 10$, is obtained from the equation

$$t_3 = \frac{2{\cdot}3 \log \frac{C_0}{C_3}}{\gamma} = \frac{2{\cdot}3 \log \frac{35{\cdot}4}{10}}{0{\cdot}00738} = 171 \text{ hours},$$

and the time, t_4, after which the current strength has sunk to half its original value, from the equation

$$t_4 = \frac{2{\cdot}3 \log \frac{C_0}{\frac{1}{2}C_0}}{\gamma} = \frac{2{\cdot}3 \log 2}{\gamma} = \frac{2{\cdot}3 \times 0{\cdot}301}{0{\cdot}00738} = 93{\cdot}8 \text{ hours}.$$

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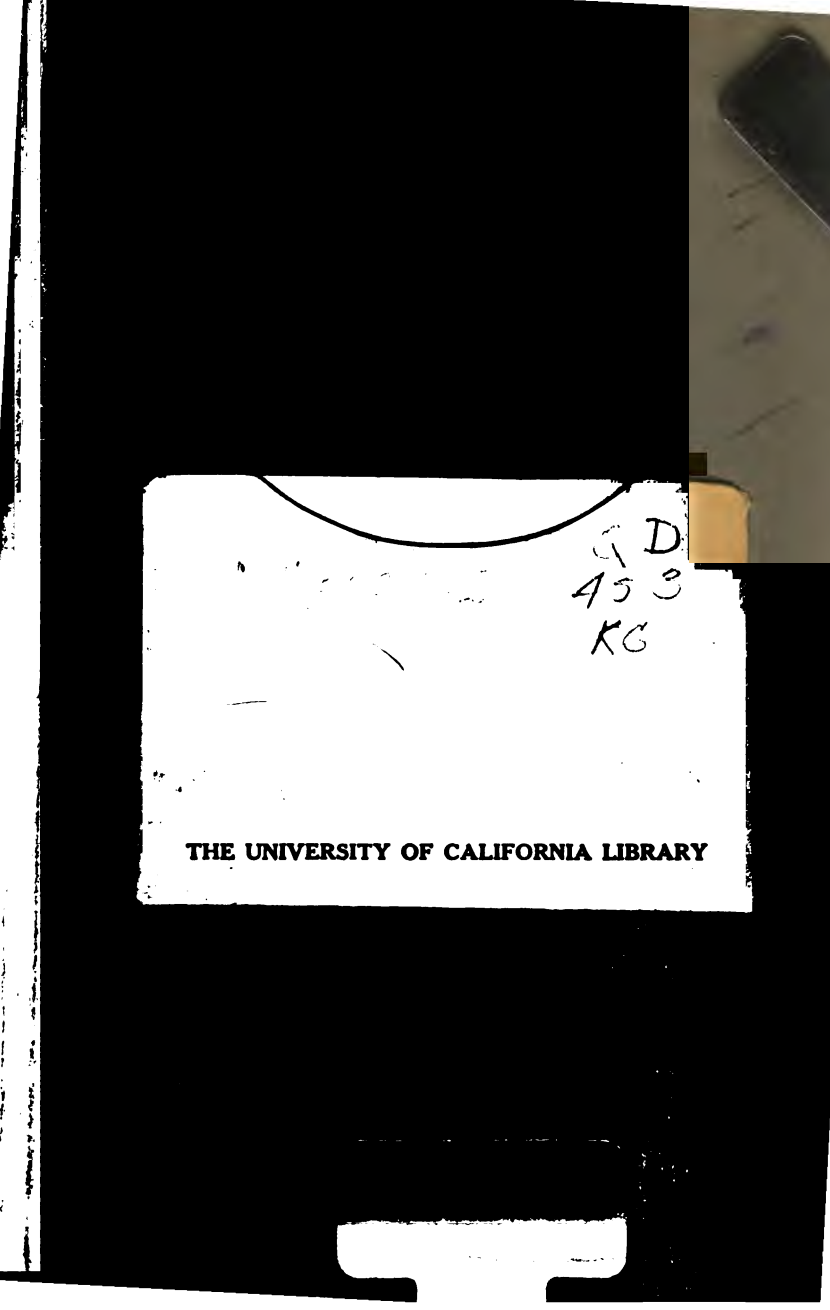
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